

A Guide to Practical Radio/ chemistry

Mir Publishers Moscow

Vol.1

«Руководство
к практическим
занятиям
по
радиохимии»

Под редакцией
чл.-корр. АН СССР
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Москва
«Химия» 1980

A Guide to Practical Radiochemistry

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of Sciences
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Vol.1

Translated
from
the Russian
by G.Leib

**Mir
Publishers
Moscow**

First published 1984

Revised from the 1980 Russian edition

На английском языке

TO THE READER

Mir Publishers would be grateful for your comments on the content, translation and design of this book. We would also be pleased to receive any other suggestions you may wish to make.

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USSR

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Preface

This two-volume collection of experiments, each accompanied by a short theoretical introduction, deals with the main branches of radiochemistry—general radiochemistry, the chemistry of nuclear transformations, the chemistry of radioactive elements, and applied radiochemistry—included in the general radiochemistry curricula and in a number of other practical courses.

The general introduction outlines certain basic concepts, discusses safety conditions and general rules for work with radioactive isotopes, and describes the design of a laboratory.

For convenience, the English translation has been divided into two volumes. The first one contains the introduction, parts one and two, and the appendices; the second volume contains parts three and four.

Part one treats experiments in general radiochemistry—the state of radioactive isotopes and elements in dilute solutions, ion and isotope exchange, coprecipitation and adsorption, extraction, and the electrochemistry of radioactive isotopes and elements.

Part two deals with experiments in the chemistry of nuclear transformations, the separation and concentration of radioactive isotopes and elements, and the change in radioactive substances that is caused by their own radiation.

Part three is devoted to the chemistry of radioactive

elements. It contains experiments in the chemistry of technetium, uranium, thorium and the products of their radioactive transformations, and also in the chemistry of neptunium and plutonium.

Part four consists of experiments involving the use of radioactive isotopes in analytical, physical, inorganic, and organic chemistry.

The introductions to the chapters and individual experiments are not intended as complete discussions of the relevant branch of radiochemistry, but contain only the basic information needed to understand the experiments. These introductions in no way replace textbooks on radiochemistry.

Some of the numerous experiments in the book duplicate one another. This allows the instructor to assign experiments according to the number of hours allocated to the course and to the interests and specialization of the students. Also, the large number of experiments devoted to each subject makes it possible to study a particular branch of radiochemistry more deeply by performing all the experiments offered in the relevant chapter.

Before beginning an experiment, students must carefully study the introduction, which sets out the basic conditions and rules for working with radioactive isotopes. Safety rules are not treated in the descriptions of the experiments, therefore students must plan the experiments in accordance with the detailed instructions contained in the introduction.

The book has been written by members of the staff of the radiochemistry department of the chemical faculty at the Moscow State University (A. M. Babeshkin, S. S. Berdonosov, I. O. Bogatyrev, E. S. Filatov, L. P. Firsova, I. V. Golubtsov, B. Z. Iofa, V. I. Korobkov, V. B. Lukyanov, I. V. Melikhov, An. N. Nesmeyanov, E. F. Simonov, E. A. Soldatov, Yu. N. Sychev, A. V. Tseplyaeva, V. K. Vlasov, K. B. Zaborenko—introduction, Chapters 1-

8, 13, 16-19) in collaboration with members of the departments of electrochemistry (A. M. Afanasyev—Chapter 9) and inorganic and analytical chemistry (A. I. Busev, K. M. Dunaeva, L. I. Martynenko—Chapters 11 and 12) of the university, and with members of the Institute of Physical Chemistry (A. F. Kuzina—Chapter 10) and the Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences (A. I. Moskvina—Chapters 14 and 15).

Individual experiments were contributed by members of the radiochemistry department of the Leningrad State University's chemical faculty (V. A. Ishina, L. D. Markarov, V. D. Nefedov, E. N. Sinotova, M. A. Toropova—Experiments 2.3, 2.12, 4.1b, 6.1, 17.4E, 17.5A, D, 19.1a), the Lensovet Leningrad Chemical Engineering Institute (V. P. Shvedov—Experiment 15.9), the Mendeleev Moscow Chemical Engineering Institute (V. N. Shamaev—Experiments 17.2, 17.4B-D), the Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences (S. S. Rodin—Experiments 13.6-13.9), and the Gorky University (Experiments 2.5, 4.1A, 8.2). Some of these experiments were substantially revised by staff members of the radiochemistry department of the chemical faculty of the Moscow State University.

Also helpful were works by An. N. Nesmeyanov, V. I. Baranov, K. B. Zaborenko, N. P. Rudenko, and Yu. A. Priselkov, *Prakticheskoe rukovodstvo po radiokhimii* (A Practical Guide to Radiochemistry), and by K. B. Zaborenko, B. Z. Iofa, V. B. Lukyanov, and I. O. Bogatyrev, *Metody radioaktivnykh indikatorov v khimii* (The Method of Radioactive Tracers in Chemistry) from which the authors took a number of experiments; most of them were substantially revised.

The book was compiled by Prof. An. N. Nesmeyanov, Associate Member of the USSR Academy of Sciences, D.Sc. (Chem.), who was also its general editor.

In the second Russian edition, certain unimportant experiments were omitted, and some new ones reflecting the state of the arts in radiochemistry were introduced. Other experiments were revised and clarified. The introduction was revised quite substantially, and the sections in it on radiation safety were checked for conformity to the new standards and regulations.

References are given at the end of each chapter. Some books for supplementary reading on the subject are listed at the end of the introduction.

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Introduction [1-3]

Radiochemistry is the field of chemistry dealing with the chemistry of radioactive isotopes, elements, and substances, the laws of their physicochemical behaviour, the chemistry of nuclear transformations, and with the physicochemical processes attending them.

Applied radiochemistry includes the synthesis of labelled compounds and the use of radioactive isotopes in science and industry.

With a view to radioactive elements and isotopes being what is studied by radiochemistry, account must be taken of the specific nature of work with radioactive substances. Three main features of work with radioactive isotopes can be earmarked:

1. Radioactive isotopes and elements in the majority of cases are prepared and used in ultramminute amounts that do not lend themselves to weighing.

2. The amount of a radioactive isotope is determined according to its activity, i.e. to the rate of decay of its nuclei.

3. Radioactive isotopes are sources of ionizing radiation that may have a harmful effect on one's organism.

Before beginning to study radiochemistry, one must study the laws of radioactive transformations, the properties of various kinds of radioactive radiation, and how to measure them. An experimenter must know and observe the rules of working with radioactive substances, and must know the fundamentals of radiation safety.

FUNDAMENTAL CONCEPTS AND UNITS

A **radioactive element** is defined to be a collection of radioactive atoms with the same charge of the nucleus, i.e. a collection of radioactive isotopes of one element.

A **radioactive isotope** is a species of radioactive atoms with the same charge of the nucleus and the same mass.

The **radioactivity (activity)** of a radioactive substance is a measure of the amount of the radioactive substance expressed by the number of events of nuclear transformations in unit time. The mass of a radioactive isotope and its activity in disintegrations per second (dps) are related by the equation

$$A = 6.02 \times 10^{23} \frac{m}{M} \lambda \quad (0.1)$$

where m is the mass of the radioactive isotope, g; M is the mass number of the isotope, g; λ is the radioactive decay constant, s^{-1} ; and 6.02×10^{23} is the Avogadro constant, atom/mol.

The SI unit of activity is a nuclear transformation per second. This unit has been named the **becquerel (Bq)**. It is recommended to use the following multiple units of the becquerel:

exabecquerel	1 EBq = $10^{18} s^{-1}$
petabecquerel	1 PBq = $10^{15} s^{-1}$
terabecquerel	1 TBq = $10^{12} s^{-1}$
gigabecquerel	1 GBq = $10^9 s^{-1}$
megabecquerel	1 MBq = $10^6 s^{-1}$
kilobecquerel	1 kBq = $10^3 s^{-1}$

Prior to January 1, 1980, in addition to the SI unit—the becquerel, a non-SI unit of radioactivity was in use—the curie (Ci), $1 \text{ Ci} = 3.700 \times 10^{10} \text{ Bq}$ (exactly). The curie and its submultiples—the millicurie (mCi, $1 \text{ mCi} = 10^{-3} \text{ Ci}$) and the microcurie (μCi , $1 \mu\text{Ci} = 10^{-6} \text{ Ci}$) were used in all previously published textbooks and reference books, and the standard documents relating to work with radioactive isotopes were based on them.

The activity expressed in becquerels or curies is known as the **absolute activity**. In most experiments using measuring instruments, what is determined is not the absolute activity A , but a quantity proportional to it, for example, the counting rate I :

$$I = \varphi A \quad (0.2)$$

The proportionality factor φ is called the counting coefficient, and it remains constant in a given series of measurements.

The **specific radioactivity (activity)** is the relative content of radioactive isotope atoms in an isotopic mixture of an element, or the fraction of molecules of the given species containing atoms of a given radioactive isotope. The specific activity is expressed by the number of activity units per unit of mass or volume: Bq/kg (Ci/kg), Bq/mol (Ci/mol), Bq/ml (Ci/ml), or Bq/cm³ (Ci/cm³). In practical work, the specific activity is frequently expressed in relative units, e.g. cpm/g [count/(min·g)] and cpm/ml [count/(min·ml)]. When using relative quantities to characterize the amount of a radioactive isotope or its specific activity, one must remember that the found values hold only for identical conditions of measurement and, consequently, depend on the way of measuring.

Radioactive isotopes are capable of emitting charged particles (electrons, positrons, alpha-particles, protons), neutral particles (neutrons and neutrinos), and photons (gamma-quanta and X-rays). Depending on how radiation interacts with a substance, we distinguish direct and indirect ionizing radiation.

Direct ionizing radiation consists of charged particles having a kinetic energy sufficient to ionize other particles they collide with.

Indirect ionizing radiation consists of uncharged particles or photons, or both, that can release directly ionizing particles or cause nuclear transformations. Ionizing radiation is characterized by the magnitude of the flux and flux density, the energy flux, and the level of the radiation flux.

The **flux of particles or photons** Φ is the ratio of the number of particles or photons ΔN penetrating into the volume of an elementary sphere with a cross-sectional area of ΔS

to this area:

$$\Phi = \frac{\Delta N}{\Delta S} \left[\frac{\text{particle}}{\text{m}^2} \left(\frac{\text{particle}}{\text{cm}^2} \right)^* \right] \quad (0.3)$$

For the particular case of a parallel beam of radiation, the flux is determined as the number of particles or photons ΔN intersecting the area ΔS oriented normally to the direction of motion of the particles or photons.

The **flux density (fluence)** is the increment of the flux $\Delta\Phi$ during the time Δt :

$$F = \frac{\Delta\Phi}{\Delta t} = \frac{\Delta N}{\Delta S \Delta t} \left[\frac{\text{particle}}{\text{m}^2 \cdot \text{s}} \left(\frac{\text{particle}}{\text{cm}^2 \cdot \text{s}} \right) \right] \quad (0.4)$$

The **radiant energy flux E** is the sum of the energies, excluding the rest energy of particles, that penetrate into a sphere with a cross-sectional area of ΔS :

$$E = \frac{\Delta N}{\Delta S} \sum_i p_i E_i = \Delta\Phi \sum_i p_i E_i \left[\frac{\text{J}}{\text{m}^2} \left(\frac{\text{MeV}}{\text{cm}^2} \right) \right] \quad (0.5)$$

where p_i is the relative content of particles or photons with the energy E_i in the spectrum.

The **radiation-flux level (flux level) J** is the increment of the energy flux during the time Δt :

$$J = \frac{\Delta E}{\Delta t} = \Delta F \sum_i p_i E_i \left[\frac{\text{W}}{\text{m}^2} \left(\frac{\text{MeV}}{\text{cm}^2} \right) \right] \quad (0.6)$$

The concept "absorbed dose" is used for a quantitative appraisal of the action of ionizing radiation on a substance, including a biological tissue.

The **absorbed dose D_{abs}** is the mean energy ΔE of any ionizing radiation transferred by it to any substance of mass Δm :

$$D_{\text{abs}} = \frac{\Delta E}{\Delta m} \quad (0.7)$$

The unit of absorbed dose is the joule/kilogram (J/kg). This SI unit has been named the **gray (Gy)**. It is recommend-

* Here and below, the first units are SI ones, and the second units, in parentheses, are non-SI ones. They are given because they were widely used in reference literature and textbooks published earlier.

ed to use units of the absorbed dose that are multiples or submultiples of the gray:

teragray	1 TGy = 10^{12} J/kg
gigagray	1 GGy = 10^9 J/kg
megagray	1 MGy = 10^6 J/kg
kilogray	1 kGy = 10^3 J/kg
milligray	1 mGy = 10^{-3} J/kg
microgray	1 μ Gy = 10^{-6} J/kg

Up to January 1, 1980, the non-Si unit "rad" (an acronym formed from the words "radiation absorbed dose") was also used in addition to the gray:

$$1 \text{ rad} = 100 \text{ erg/g} = 0.01 \text{ J/kg} = 0.01 \text{ Gy}$$

The absorbed dose unit rad and its derivatives were used in all previously published textbooks and reference books, and the standard documents regulating work with radioactive isotopes are based on them.

The direct measurement of the absorbed dose in most cases is difficult to perform because of the too low heat effect produced by ionizing radiation in doses close to the safe ones. This is why indirect methods are used to measure the absorbed dose; for example, the ionization produced by photons in the air or the flux of the energy of corpuscular radiation is measured with subsequent conversion of the values obtained to the absorbed dose.

The **exposure (exposure dose)** D_{exp} is the absolute value of the total charge of the ions of one sign ΔQ that are formed in air upon the complete deceleration of the electrons and positrons released by photons in an element of volume of air with the mass Δm :

$$D_{\text{exp}} = \frac{\Delta Q}{\Delta m}$$

The SI unit of exposure is the coulomb/kilogram (C/kg). A non-Si unit is the **roentgen (R)**—the total charge (in cgse_q units) of the ions formed in 1 cm^3 of air at standard atmospheric pressure and a temperature of 25°C :

$$1 \text{ R} = 2.58 \times 10^{-4} \text{ C/kg}$$

When the energy of photons transferred to charged particles equals the energy transferred by the charged particles to

the atoms and molecules of the air (i.e. there is electron equilibrium), the exposure equals the absorbed dose. To determine the relation between the units of the absorbed dose and the exposure, we must find the energy equivalent of the roentgen. It can be determined if we know the concentration of the ions in the air, their charge and the energy spent to form an ion pair. Assuming all the ions to be singly charged ($e = 4.8 \times 10^{-10}$ cgs $_q$) and an average of 34 eV to be spent for the formation of one pair of ions in the air, we obtain:

$$\begin{aligned}\text{Energy equivalent} &= \frac{1 \times 34}{1 \times 4.8 \times 10^{-10}} \\ &= 7.08 \times 10^{10} \text{ eV/cm}^3 \\ &= 7.08 \times 10^{10} \times 1.6 \times 10^{-12} \\ &= 0.114 \text{ erg/cm}^3 = 0.114/1.293 \times 10^{-3} = 88 \text{ erg/g}\end{aligned}$$

where 1.6×10^{-12} is a conversion factor for converting electron-volts to ergs; 1.293×10^{-3} g/cm 3 is the density of air at standard temperature and pressure.

Hence, in conditions of electron equilibrium in the air, the exposure can be converted to the **absorbed dose** by the equation

$$D_{\text{abs}} = 0.88 D_{\text{exp}}$$

where D_{exp} is measured in R; D_{abs} is measured in rad; and 0.88 is a proportionality factor, rad/R.

The absorbed dose (in rad) in any substance can be determined, if we know the exposure (in R), by the equation

$$D_{\text{abs}} = 0.88 \frac{\mu'_e(Z)}{\mu'_e(\text{air})} D_{\text{exp}} \quad (0.8)$$

where $\mu'_e(Z)$ and $\mu'_e(\text{air})$ are the mass coefficients of the true absorption of photons in a substance with the atomic number Z and in air.

The **dose rate** P is the increment of the absorbed dose or the exposure ΔD during the time Δt :

$$P = \frac{\Delta D}{\Delta t} \quad (0.9)$$

The dose rate of photon or corpuscular radiation can also be determined according to the flux level or the flux density:

$$P = 1.6 \times 10^{-8} f(E, Z) F [\text{rad/s}] \quad (0.10)$$

where $f(E, Z)$ is a function relating the flux density for particles of a given species and the dose rate; and 1.6×10^{-8} is a proportionality factor, (rad·g)/MeV.

For example, for monoenergetic photons, the dose rate is

$$P = 1.6 \times 10^{-8} E_{\gamma, 0} \mu'_e(Z) F_{\gamma, 0} [\text{rad/s}] \quad (0.11)$$

where

$$f(E, Z) = E_{\gamma, 0} \mu'_e(Z) \{ (J \cdot m^2)/kg [(MeV \cdot cm^2)/g] \}$$

The biological action of various kinds of ionizing radiation is not the same because of the difference in the mechanism of transferring the energy of the ionizing radiation to the biological tissue. At doses close to the maximum permissible ones and upon the prolonged action of radiation of an arbitrary composition on an organism, the concept of the equivalent dose is introduced.

The **equivalent dose** D_{eq} is the sum of the products of the absorbed doses D_i of separate kinds of radiation in a biological tissue and the corresponding values of the quality coefficients $K_{q,i}$ for these kinds of radiation:

$$D_{eq} = \sum_i D_i K_{q,i} \quad (0.12)$$

A special unit of the equivalent dose is the **rem** (roentgen-equivalent-man).

Table 0.1. Quality Coefficients for Various Kinds of Ionizing Radiation

Kind of radiation	L.E.T. in water, keV/ μm	K_q
Gamma-radiation	≤ 3.5	1
X-rays		
Electrons and positrons		
Beta-radiation		
Protons ($E \leq 10$ MeV)	≈ 53	10
Heavy recoil nuclei and alpha-radiation ($E \leq 10$ MeV)	≈ 175	20
Thermal neutrons	≈ 15	3
Fast neutrons ($E = 1$ MeV)	≈ 53	10
Ditto ($E = 10$ MeV)	≈ 30	6.5

The **quality coefficient** K_q is a quantity determining how the biological effect of chronic irradiation of an organism by a given kind of ionizing radiation depends on the magnitude of the linear energy transfer (L.E.T.) of this kind of radiation (see Table 0.1).

Example. Determine the equivalent dose in a mixed field of gamma- and n -radiation if the dose of γ -radiation is $D_\gamma = 5.0$ mrad, the dose of thermal neutrons is $D_{th.n} = 0.2$ mrad, and the dose of fast neutrons is $D_{f.n} = 1.0$ mrad (for $E_{f.n} = 1$ MeV).

Solution. The equivalent dose is calculated by Eq. (0.12) and according to the data of Table 0.1:

$$\begin{aligned} D_{eq} &= \sum_i D_i K_{q,i} \\ &= D_\gamma K_{q,\gamma} + D_{th.n} K_{q,th.n} + D_{f.n} K_{q,f.n} \\ &= 5.0 \text{ mrad} \times 1 + 0.2 \text{ mrad} \times 3 \\ &\quad + 1.0 \text{ mrad} \times 10 = 15.6 \text{ mrem} \end{aligned}$$

RADIATION SAFETY STANDARDS WHEN WORKING WITH RADIOACTIVE ISOTOPES

Work with sources of ionizing radiation, including radioactive isotopes, must be organized so as to render no harm to the health of the workers themselves and of persons who may accidentally or briefly be in the zone of action of the radiation. Radiation safety standards and rules for working with sources of ionizing radiation are worked out on the basis of recommendations of the International Committee on Radiological Protection, the National Committee on Radiological Protection, and after approval by the relevant state organs are the basic documents regulating work with radiation sources and protection against ionizing radiations.

In working out the radiation safety standards, account is taken of the possibility of external and internal irradiation of an organism.

External irradiation is the action on an organism of ionizing radiations from radiation sources outside it.

Internal irradiation is the action on an organism of the ionizing radiations of radioactive substances that are inside the organism. Radioactive substances getting into an organism, depending on the species of the isotope and on the chemical and physical states of the radioactive substance,

may selectively accumulate in an internal organ. An organ, tissue, part of a body, or the entire body whose irradiation in the given conditions causes the greatest harm to the health of the given person or his or her offspring is known as the **critical organ**. Critical organs are grouped according to their radiosensitivity. Depending on the possible consequences of the influence of ionizing radiations on an organism, the Radiation Safety Standards (NRB-76) in force in the USSR establish the following categories of irradiated persons:

Category A—staff (professional workers)—persons who work directly with sources of ionizing radiations or who according to the nature of their work may be irradiated.

Category B—a limited portion of the population—persons who do not work directly with sources of radiation, but who according to the location of their residences or the location of their workplaces may be subjected to the action of radioactive substances and other sources of radiation.

Category C—the population as a whole (in appraising the genetically significant radiation dose).

For category A, the maximum permissible dose (MPD) is established. It equals the annual level of radiation that upon the uniform accumulation of the dose during 50 years of work causes no unfavourable changes in the state of health of the irradiated person himself and his offspring that can be detected by modern methods of control. For category B, the maximum dose is established—the permissible annual level of irradiation of individuals of the population. It is one-tenth of the MPD for category A.

The maximum permissible doses are established for three groups of the critical organs or tissues:

group I—the entire body, the gonads, and red bone marrow;

group II—the muscles, crystalline lens of the eye, gastrointestinal tract, liver, kidneys, pancreas, lungs, adipose tissue, thyroid gland, and other organs except those relating to groups I and III;

group III—the bone tissue, skin, hands, forearms, ankles, and feet.

For each group of critical organs, the maximum permissible doses (somatic) of external and internal irradiation of the staff and the maximum doses for individual persons from among the population are established:

Group of critical organs	I	II	III
Maximum permissible dose (MPD) for category A, rem/year	5	15	30
Maximum doses for category B, rem/year . . .	0.5	1.5	3

Note. For category A (except for women up to 40 years old) the distribution of the dose of external radiation during the year is not regulated. For women up to 40 years old, the dose in the region of the pelvis must not exceed 1 rem during any two months.

For operative dosimetric control of the levels of external radiation, the maximum permissible values of the dose rates (MPDR) are used. They are obtained proceeding from a working time of 1800 h a year (50 weeks a year, 6 days a week, 6 h a workday). In appraising safe conditions of work and in dosimetric control, one must take into account that the MPD are calculated for the simultaneous action of external and internal radiation and do not include the doses of the natural background and those obtained in medical treatment.

The radiation safety standards are observed provided that the total action of all kinds of external and internal radiation is less than or equal to the MPD for the given group of critical organs, i.e. the following condition must be satisfied:

$$\sum_{i,j} \frac{D_{i,j}}{(\text{MPD})_{ij}} \leq 1 \quad (0.13)$$

where D_i is the dose of external radiation for the given group of critical organs; D_j is the dose of internal radiation for this group of critical organs; and $(\text{MPD})_{ij}$ is the maximum permissible dose a year for the given group of critical organs.

The dose of irradiation of the entire organism, gonads, or the red bone marrow accumulated during the time of professional work by a person of category A must never exceed the value calculated by the formula

$$D = 5 (t - 18) \quad (0.14)$$

where D is the dose, rem; t is the age, years; and 18 is the age from which a person is allowed to work with ionizing radiation according to Soviet legislation (if the laws of your country provide for a different age, it must be inserted into formula 0.14 instead of 18).

The level of irradiation can be controlled by using the values of the maximum permissible flux densities (MPFD), which are equivalent to the maximum permissible dose rates (Table 0.2).

Table 0.2. Maximum Permissible Flux Densities (in $\text{cm}^{-2}\text{s}^{-1}$) of Photons, Electrons, and Neutrons Corresponding to $\text{MPD} = 0.1 \text{ rem/week}$ at 36 Working Hours a Week

Radiation energy, MeV	Photons	Electrons	Neutrons	Radiation energy, MeV	Photons	Electrons	Neutrons
0.025×10^{-6}	—	—	750	0.5	3 250	24.2	33
0.1×10^{-6}	—	—	550	0.6	2 720	25.0	—
0.005	—	—	640	0.8	2 086	26.0	—
0.020	4 670	—	310	1.0	1 720	26.3	—
0.1	20 700	11.9	90	1.5	1 260	26.0	—
0.2	9 000	17.6	—	3.0	762	25.4	—
0.3	5 580	20.9	—	10.0	315	22.6	20
0.4	4 070	22.9	—				

Example. A radiometer was used to measure the densities of fluxes of: γ -radiation with $E_\gamma = 0.6 \text{ MeV}$, $F_\gamma = 1300 \text{ cm}^{-2}\text{s}^{-1}$, thermal neutrons $F_{\text{th. n}} = 30 \text{ cm}^{-2}\text{s}^{-1}$, and fast neutrons $F_{\text{f. n}} = 10 \text{ cm}^{-2}\text{s}^{-1}$. Determine the equivalent dose rate in a soft biological tissue if $\text{MPDR} = 2.8 \text{ mrem/h}$.

Solution. The ratio of the measured flux density to the MPFD for each kind of radiation is a quantity showing how many times the dose rate of the given radiation exceeds the maximum permissible value. Using the data contained in Table 0.2, we have:

$$\begin{aligned}
 P_{\text{eq}} &= \left[\frac{F_\gamma}{(\text{MPFD})_\gamma} + \frac{F_{\text{th. n}}}{(\text{MPFD})_{\text{th. n}}} + \frac{F_{\text{f. n}}}{(\text{MPFD})_{\text{f. n}}} \right] \times \text{MPDR} \\
 &= \left(\frac{1300}{2720} + \frac{30}{750} + \frac{10}{20} \right) \times 2.8 \text{ mrem/h} = 2.85 \text{ mrem/h}
 \end{aligned}$$

Shielding from external irradiation by penetrating ionizing radiation (photons, neutrons, high-energy charged particles) must be designed with a view to the time spent by the staff in the relevant premises and to the possibility of internal irradiation. The dose rates on the surface of the shielding must never exceed the values indicated in Table 0.3.

Table 0.3. Dose Rate Used in Designing Shielding from External Fluxes of Ionizing Radiations

Category of irradiated persons	Premises	Design dose rate, mrem/h	
		$t = 36$ h/week	$t = 41$ h/week
A	Controlled Zone		
	1. Premises with constant presence of working staff ($> 50\%$ of working time)	1.4	1.2
	2. Premises with temporary presence of staff ($< 50\%$ of working time)	2.8	2.4
	3. Premises with no attendance	28	24
B	4. Any other premises in controlled zone	0.1	0.1
	Watched Zone		
	Any premises and territory within the confines of the watched zone	0.03	0.03

With known doses of internal irradiation or when other factors of radiation action are present (for example, the presence of other sources in the same working premises), the design dose rate must be lowered accordingly.

The values of the MPD given on p. 26 are the basis for calculating the maximum permissible content (MPC) of radioactive isotopes in an organism and the related quantities—the maximum permissible entry (MPE) and the mean annual permissible concentration (APC) of radioactive isotopes in the air of working premises. Table 0.4 gives the values of the MPC, MPE, and APC for selected isotopes.

The differences in the values of the maximum permissible quantities characterizing radioactive isotopes as sources of internal irradiation are associated with their different radiotoxicity. The radioactivity of an isotope is higher when the values of the maximum permissible quantities characterizing it as a source of internal irradiation are lower. The radiotoxicity depends on the effective energy of decay of a radioactive isotope, the critical organ in which the isotope accumulates, and on the effective half-life of the isotope in the organism. In the general case, the radiotoxicity of alpha-radiation is higher than that

Table 0.4. Content of Radioactive Isotopes in Organs or Tissues Corresponding to MPD for Staff (MPC), Annual Maximum Permissible Entry (MPE), and Mean Annual Permissible Concentration (APC) in Air of Working Premises

Isotope	Critical organs	MPC, μCi	MPE, $\mu\text{Ci/year}$	APC, Ci/litre
^3H ($^3\text{H}_2\text{O}$)	Body's tissues	1.2×10^3	1.2×10^1	4.8×10^{-9}
^{14}C (s)*	Adipose tissue	1.6×10^3	8.7×10^3	3.5×10^{-9}
^{21}Na (s)	Gastro-intestinal tract	—	3.1×10^3	1.4×10^{-10}
^{32}P (s)	Bone tissue	3.1	1.8×10^2	7.2×10^{-11}
^{35}S (s)	Gonads	0.2	6.8×10^2	2.5×10^{-10}
^{59}Fe (s)	Spleen	0.37	3.7×10^2	5.2×10^{-11}
^{60}Co (s)	Entire organism	13	8.7×10^2	8.8×10^{-12}
^{90}Sr (s)	Bone tissue	3.9	69	2.8×10^{-11}
^{90}Sr (s)	Ditto	2.0	2.9	1.2×10^{-12}
^{95}Nb (s)	Entire organism	38	1.2×10^3	1×10^{-10}
^{110}Ag (s)	Gastro-intestinal tract	—	4.8×10^2	1.0×10^{-11}
^{131}I (s)	Thyroid gland	0.15	21	8.4×10^{-12}
^{137}Cs (s)	Entire organism	33	1.6×10^2	1.4×10^{-11}
^{203}Hg (s)	Kidneys	1.7	1.8×10^2	7.2×10^{-11}
^{210}Po (s)	Ditto	0.025	0.31	1.2×10^{-13}
^{210}Po (s)	Spleen	0.0020	1.2	2.0×10^{-13}
^{226}Ra (s)	Bone tissue	0.10	0.71	1.0×10^{-13}
^{239}Pu (s)	Ditto	0.041	4.3×10^{-3}	1.7×10^{-15}
^{239}Pu (is) **	Lungs	0.016	9.5×10^{-2}	1.7×10^{-15}

* s = isotope in soluble state.

** is = isotope in insoluble state.

of beta-emitters because the radiation quality coefficients K_q for these two sources of radiation are 20 and 1, respectively.

In connection with the fact that when working with radioactive isotopes, in addition to external irradiation there is a hazard of a radioactive substance getting into an organism, sources of ionizing radiation are divided into bare and shielded (encapsulated) ones. A **bare radioisotope source of radiation** is a source whose use may be attended by radioactive substances getting into the surroundings. A **shielded radioisotope source of radiation** is a source whose design excludes the entry of radioactive substances into the surroundings in foreseen conditions of its service and wear.

The working rules and equipment of premises for work with radioactive isotopes in the bare and shielded states

are different. The performance of work in practical radiochemistry is associated with the use of radioactive isotopes in the bare form. The performance of work with sources of ionizing radiation in the USSR is regulated by the "Basic Sanitary Rules for Working with Radioactive Substances and Other Sources of Ionizing Radiations" (OSP-72), and also by internal instructions taking into consideration the specific nature of the work. The internal instructions must never contradict the standards NRB-76 and the instructions OSP-72. Permission for conducting work with sources of ionizing radiations are drawn up by the sanitary and epidemiological service after checking the correspondence of the conditions of performing the work to the requirements of NRB-76 and OSP-72.

Bare radioactive substances, as potential sources of internal irradiation, are divided into five groups of radiotoxicity. The inclusion of a radioactive isotope in a radiotoxicity group is determined by NRB-76 depending on the maximum permissible activity at a workplace not requiring registration or the obtaining of permission from the sanitary-epidemiological service (SES).

Group A—elements with an especially high radiotoxicity. This group includes isotopes for which the activity requiring no permission from the SES is 0.1 μCi :

^{210}Pb , ^{210}Po , ^{211}At , ^{226}Ra , ^{228}Ra , ^{227}Ac , ^{228}Th , ^{230}Th ,
 ^{231}Pa , ^{232}U , ^{237}Np , ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{242}Pu , ^{244}Pu ,
 ^{241}Am , ^{242}Cm , ^{252}Cf , etc.

Group B—elements with a high radiotoxicity. This group includes isotopes for which the activity not requiring permission from the SES is 1 μCi :

^{90}Sr , ^{106}Ru , ^{121}Sb , ^{126}I , ^{131}I , ^{144}Ce , ^{210}Bi ,
 ^{223}Ra , ^{224}Ra , ^{227}Th , ^{230}Pa , ^{235}U , ^{241}Pu , etc.

Group C—elements with a moderate radiotoxicity. This group includes isotopes for which the activity not requiring permission from the SES is 10 μCi :

^{22}Na , ^{24}Na , ^{32}P , ^{35}S , ^{36}Cl , ^{45}Ca , ^{47}Sc , ^{52}Mn , ^{54}Mn ,
 ^{59}Fe , ^{57}Co , ^{60}Co , ^{63}Ni , ^{65}Zn , ^{72}Ga ,
 ^{73}As , ^{82}Br , ^{89}Sr , ^{90}Y ,
 ^{95}Zr , ^{95}Nb , ^{99}Tc , ^{110m}Ag , ^{133}I , ^{137}Cs , ^{140}Ba , ^{140}La ,
 ^{141}Ce , ^{182}Ta , ^{181}W , ^{185}W , ^{203}Pb , ^{206}Bi , etc.

Group D—elements with a low radioactivity. This group includes isotopes for which the activity requiring no permission from the SES is 100 μCi :

^7Be , ^{11}C , ^{38}Cl , ^{51}Cr , ^{55}Fe , ^{64}Cu , ^{69}Zn ,
 ^{71}Ge , ^{97}Zr , ^{136}Cs , ^{193m}Pt , ^{197}Hg , ^{200}Tl , etc.

Group E—this group includes isotopes for which the activity requiring no permission from the SES is 1000 μCi — ^3H .

Notes. 1. The maximum permissible amount of ^{238}U and ^{232}Th at a workplace that requires no registration or permission from the SES must never exceed 1.0 kg.

2. When working with a natural mixture of uranium isotopes, have in view that 1 kg of natural uranium contains 333 μCi of ^{238}U , 15.3 μCi of ^{235}U (group B), and 337 μCi of ^{234}U (group B). Work with ^{235}U and ^{234}U is controlled according to the activity, and not according to the mass.

3. When working with minerals, ores, and other natural objects containing isotopes of the uranium and thorium series, the degree of radioactive equilibrium of the system must be established and the class of work determined according to the most radiotoxic isotope.

CLASSIFICATION OF WORK WITH BARE RADIOACTIVE ISOTOPES

All work with bare radioactive isotopes is divided into three classes (Table 0.5). The class of work determines the

Table 0.5. Classes of Work with Bare Radioactive Isotopes

Radiotox- icity group	Maximum permis- sible radioactivity at workplace not requiring permission from SES, μCi	Activity at workplace, μCi		
		Class I	Class II	Class III
A	0.1	over 10^4	10 - 10^4	0.1 - 1.0
B	1.0	" 10^5	10^2 - 10^5	1 - 10^2
C	10.0	" 10^6	10^3 - 10^6	10 - 10^3
D	100.0	" 10^7	10^4 - 10^7	10^2 - 10^4
E	1000.0	" 10^8	10^5 - 10^8	10^3 - 10^5

Notes: 1. When using radioactive isotopes whose maximum permissible activity at the workplace not requiring permission from the SES is not indicated in the standard NRB-76, adopt the value of this activity equal to 0.1 μCi .

2. The present classification has been established proceeding from the hazard for workers associated with the possibility of radioactive contamination of the air in premises without taking into account the characteristics of substances as sources of external irradiation.

requirements to the location and equipment of the premises in which work is to be performed with bare radioactive substances.

According to the degree of potential hazard of contamination of the environment, operations with radioactive isotopes can be divided into five groups.

Storage of Radioactive Substances. When storing radioactive substances, their packing must correspond to the species of the radioactive isotope and the nature of the isotope's chemical compound so that upon prolonged storage in the relevant conditions the contamination of the environment would not exceed the maximum permissible rates. The following processes lead to pollution of the environment in storage:

- the evolution of radioactive gases (emanation);

- the formation of radioactive vapours (organic compounds, halides, etc.);

- the formation of volatile radiolysis products (leads to a substantial increase in the pressure in ampoules with a radioactive solution);

- destruction of the packing because of radiation damage;

- the formation of radioactive aerosols at the expense of the recoil energy in alpha-decay and in spontaneous fission of nuclei. When storage is properly organized, the contamination of the environment is minimum.

Simple Operations with Solutions. This group includes operations such as pouring, dilution, and taking samples of radioactive aqueous solutions. Contamination of the environment mainly occurs upon careless work and can be related to accidental losses.

Ordinary Chemical Operations. This group includes operations with solutions in which the probability of contamination of the environment is increased in comparison with simple operations—precipitation, filtration, titration, centrifuging and other processes performed without heating. The use of special contrivances or laboratory equipment in performing these operations can appreciably lower contamination of the environment.

Complicated Operations with Solutions. This group includes operations associated with heating: evaporation, distillation, hot extraction and filtration, and also reactions with the evolution of gases. These operations may lead to contamination of the air and working surfaces as a result

of splashing and the mechanical carrying off of solid substances from solutions by drops of the liquid. The danger of contaminating the air with radioactive aerosols upon the boiling of radioactive solutions or drying precipitates in the air space directly over a solution or precipitate can be appraised by the equations:

$$\Delta A_{\text{air}} [\text{Ci/litre}] = 2 \times 10^{-7} \Delta A_{\text{sln}} [\text{Ci/litre}] \quad (\text{in boiling}) \quad (0.15)$$

$$\Delta A_{\text{air}} [\text{Ci/litre}] = 2 \times 10^{-7} \Delta A_{\text{s}} [\text{Ci/litre}] \quad (\text{in drying}) \quad (0.16)$$

(Here the subscripts "sln" and "s" stand for "solution" and "solid", respectively.)

Example. Determine the concentration of the isotope ^{90}Sr in the air upon the evaporation by boiling of 10 ml of a solution with the specific activity of $\Delta A = 10 \mu\text{Ci/ml}$ with the following drying. Determine the possibility of performing the operation without shielding.

Solution. 1. The specific activity of the aerosol over the solution's surface upon evaporation at the beginning of the operation is:

$$\begin{aligned} \Delta A_{\text{air}} &= 2 \times 10^{-7} \Delta A_{\text{sln}} \times 1 \times 10^{-6} \\ &= 2 \times 10^{-9} \text{ Ci/litre} \end{aligned}$$

2. The specific activity of the vapour in drying is:

$$\begin{aligned} \Delta A_{\text{air}} &= 2 \times 10^{-7} \Delta A_{\text{s}} V \times 1 \times 10^{-6} \\ &= 2 \times 10^{-11} \text{ Ci/litre} \end{aligned}$$

3. In accordance with the radiation safety standards (see Table 0.4), the APC for ^{90}Sr is $1.2 \times 10^{-12} \text{ Ci/litre}$, consequently these operations may not be performed without special measures being taken for shielding.

Operations with Dry Dust-Forming Substances and Primary Packages of Radioactive Isotopes. The greatest hazard from the viewpoint of environment contamination is work with powders of radioactive substances when dissolving or calcining them. Calcination may be attended by sublimation of radioactive substances (halides, oxides, etc.). Work with powders must be organized so as to prevent their atomization and the formation of aerosols.

Primary packages of radioactive substances contain radioactive isotopes with high specific activities, which requires special care when handling them. Upon the prolonged storage of liquid radioactive substances in soldered am-

poles, gaseous products of radiolysis may accumulate that increase the pressure in the ampoules. When the latter are opened, the ejection of radioactive substances having a high specific activity is possible.

The nature of the operations being performed must be taken into account when determining the class of the work. In work of any class, depending on the complexity of the operations performed at a workplace, it is permitted to:

(a) store radioactive substances with an activity 100 times higher than that indicated in Table 0.5;

(b) perform simple operations with liquid radioactive substances having an activity 10 times higher than that indicated in Table 0.5;

(c) perform ordinary chemical operations with an activity of the substances not exceeding that established for work of the given class;

(d) perform complicated operations with liquid radioactive substances having an activity that is one-tenth of the figure given in Table 0.5;

(e) perform operations with dry dust-forming and powdery radioactive substances having an activity that is one-hundredth of the figure given in Table 0.5.

The class of work is established depending on the group of radiotoxicity of the radioactive isotope and its actual amount (activity) at the workplace indicated in Table 0.5. When organizing work with radioactive isotopes, one must take into account that the maximum activity at a workplace in accordance with the requirements of the instructions OSP-72 may grow 1000 times when the class of the work becomes higher. The radiation safety standards are the same for all kinds of work, and, consequently, the degree of sealing of the shielding equipment to prevent contamination of the environment with radioactive isotopes should grow 1000 times when the class of the work becomes higher.

The collection of protective measures when working with the use of bare radioactive substances must ensure the prevention of contamination of the air and surfaces of the working premises, the skin and clothing of the staff (including persons working in adjacent rooms), and also objects of the environment—the air, water, soil, etc. The main prophylactic measures include the proper choice of the layout of the premises, the equipment, the finishing

of the premises, the technological conditions, the rational organization of the workplaces and observance of sanitary rules by the workers, rational systems of ventilation, gathering and disposal of the radioactive waste.

ORGANIZATION OF WORK WITH BARE RADIOACTIVE ISOTOPES

LAYOUT OF RADIOCHEMICAL LABORATORIES

In planning the layout of working premises, one should ensure sufficiently free arrangement of the workplaces (the total area per worker must be at least 10 m²), convenient arrangement of the equipment, and prevent the possibility of spreading of contamination, and also observe the principle of concentrating premises for work with radioactive substances in one part of a building or in a separate building.

Work of Class III. The layout of laboratories for work of class III does not have to meet any special requirements. It is preferable to perform this work in separate rooms, but it may also be carried out in common rooms outfitted in accordance with the requirements which chemical laboratories must meet.

In class III work, simple operations with solutions of non-volatile and non-emanating substances may be performed on separate working tables. More complicated work is performed in fume cupboards (hoods).

Balanced (suction-and-exhaust) ventilation is used with three air changes an hour and with separate ducts for the fume cupboards.

Work of Class II. This work must be performed in separate specially equipped premises isolated in a separate bay or wing of the building.

A class II laboratory must include working and auxiliary premises:

- (1) a room for storing radioactive isotopes;
- (2) a room for preliminary processing (unpacking) of radioactive preparations (these two rooms may be located in direct proximity to each other);
- (3) working rooms for performing chemical operations with radioactive substances;

(4) rooms for measuring the preparations and filling in the relevant documents;

(5) a shower room or the like for decontamination of the body;

(6) a dosimetric control facility at the exit and a locker or wardrobe for storing the personal clothing and overalls of the workers;

(7) a room for taking food and water.

The layout of a class II laboratory is in essence a two-zone one—a “clean” and a “contaminated” zones.

Other work not connected with the use of radioactive substances must never be performed in class II laboratory premises.

The air is changed from five to ten times an hour. Special and balanced ventilation is used. Filters are installed on the cupboards and boxes when necessary for purifying the air being exhausted.

Class II work with radioactive substances must be performed in fume cupboards or in glove or manipulator boxes. For work with emanating radioactive substances, a round-the-clock system of exhaust ventilation must be provided.

Work of Class I. Special laboratories are outfitted for class I work. They are located in a separate building or in an isolated wing of a building with a separate entrance only through an obligatory decontamination facility.

It is recommended to base the layout of class I laboratories on the principle of dividing the premises into three zones, proceeding from the degree of possible radioactive contamination.

First zone—location of the equipment, chambers, boxes, communications and so on that are the main sources of radioactive contamination.

Second zone—repair and handling premises, intended for loading and unloading radioactive materials, performing repairs or other auxiliary work associated with the opening and deactivation of the technological equipment.

Third zone—the zone of the operator and switchboard premises associated with the constant presence in it of most of the workers.

To fabricate technological and shielding equipment, it is necessary to use poorly sorbing materials and coatings that are stable with respect to the substances, reagents, and desorbing acid and alkaline solutions that are used.

In premises intended for class I and II work, the floors and walls, and in the repair zone and zone of equipment location also the ceilings must be coated with special poorly sorbing materials resisting detergents. The edges of floorings must be raised and sealed flush with the walls. When special sewerage is provided, the floors must have a slope and traps. The corners of rooms must be rounded off. Door leaves and window sashes must have very simple profiles.

The equipment and working furniture must have a smooth surface, simple design, and poorly sorbing coatings and finishes facilitating the removal of radioactive pollutants. The use of upholstered furniture is prohibited.

The equipment, appliances, and furniture must be assigned to premises of each class, zone, and marked accordingly. They may be transferred from one room to another only after radiometric control.

In experiments with bare radioactive substances, measures must be taken to protect the workers from external irradiation.

Radioactive Isotope Store. Radioactive substances not in use must be stored in specially assigned places or in stores excluding the access of unauthorized persons. The finishing and equipment of a store must meet the requirements to premises for work of the relevant class, but not lower than the second one. A store must be provided with exhaust ventilation functioning around the clock.

Radioactive isotopes are kept in shielding safes, recesses, or wells. The doors of the storage places must have clearly legible marking.

LABORATORY EQUIPMENT

Fume cupboards (hoods) are shelters with rising or sliding curtains or doors provided with exhaust ventilation and intended for work with radioactive substances with the use of or without gloves. The cupboards are made from materials easy to wash. A special removable filter is installed at the connection of the cupboard to a ventilation duct. The working surface of a cupboard is made in the form of a stainless steel tray.

A cupboard is provided with means for washing its internal surface and with containers for collecting liquid

and solid waste. The bottom of a cupboard is designed with a slope toward a drain and for the increased loads appearing when shielding screens are installed.

A cupboard is supplied with gas, water, compressed air, and electricity. The control panel is on the outer side of the cupboard. Each cupboard is outfitted with ventilation with an individual duct. The ventilation system must ensure the removal of the air in the lower part, which eliminates any possibility of vapour rising and then condensing on the colder upper portions of the cupboard. The bottom system of air removal also makes it possible to work with finely dispersed substances that with a vertically ascending air stream might be spread over the entire volume of the fume cupboard. The front wall is a stainless steel frame into which organic glass is inserted.

The interior of a cupboard is illuminated through a glazed window with the aid of lamps installed outside it. Figure 0.1 shows an external view of a fume cupboard with one workplace, and Fig. 0.2 shows schematically a fume cupboard with two workplaces.

Glove and manipulator boxes are movable shelters with a definite degree of sealing made from poorly sorbing materials and are intended for work with radioactive substances in a rarefied atmosphere with the use of manipulators or gloves. Two main types can be distinguished, namely, boxes intended for work with α -active substances, and with β - and γ -active substances.

Glove boxes in which chemical experiments may be performed with α -emitting substances (Fig. 0.3) in the simplest case must protect the experimenter from direct contact with these substances. Here the thin layer of the rubber gloves completely absorbs alpha-particles. A suitable material for glove boxes is organic glass, duralumin, or stainless steel with an organic glass window for observation.

The heavy manipulator boxes intended for studying β - and γ -active substances are considerably more complicated as regards their design and operation. Massive thick walls made from lead or iron are needed to absorb gamma-radiation. Such a box is outfitted with various kinds of manipulators instead of with gloves. Most heavy boxes are designed so as to exclude the direct contact of an experimenter with radioactive substances. This is why neither the front nor the side walls of a box have doors through which the inter-

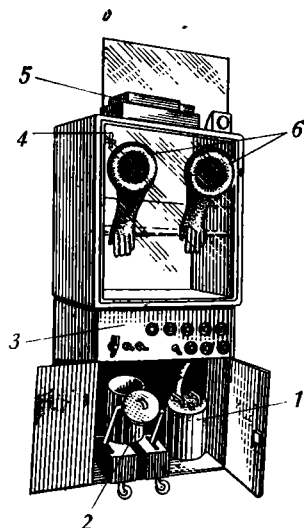


Fig. 0.1.

Metal fume cupboard with one workplace:

1—collector of liquid waste; 2—collector of solid waste;
3—panel for controlling electric current, water, gas, etc.;
4—rising organic glass door; 5—filter; 6—rubber gloves

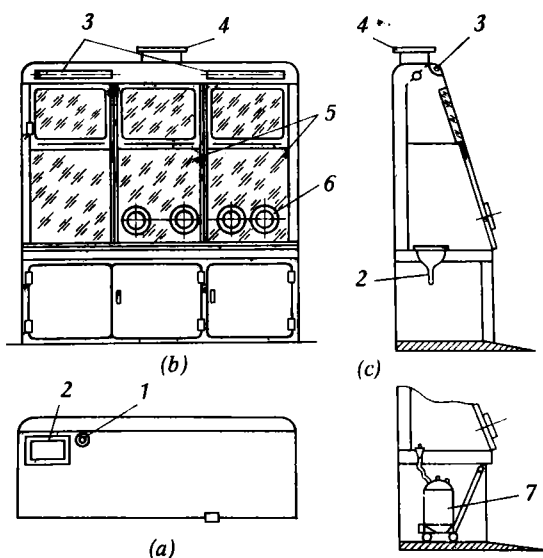


Fig. 0.2.

Fume cupboard with two workplaces:

a—top view toward cupboard table; b—front wall of cupboard; c—side view; 1—water inlet; 2—sink; 3—daylight lamps; 4—opening for connection to ventilation duct; 5—rising organic glass doors; 6—openings for gloves; 7—collector of liquid waste

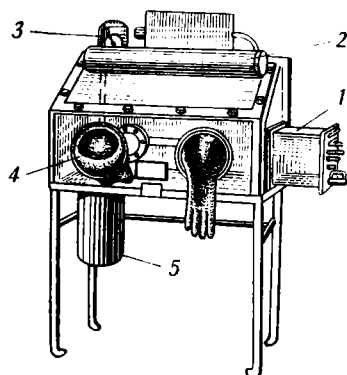


Fig. 0.3. Organic glass glove box for work with α -active substances:

1—prechamber for loading and unloading box; 2—lamp; 3—pressure gauge; 4—rubber gloves; 5—collector of solid waste

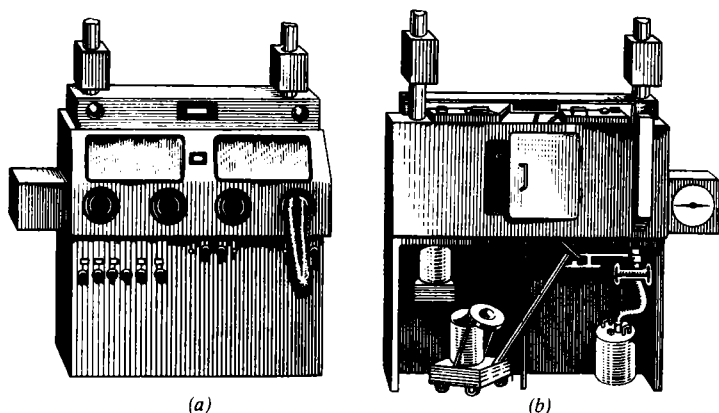


Fig. 0.4. Metal manipulator box with two workplaces for work with β - and γ -emitters:

a—view from side of operator's workplace; b—view from side of repair zone

nal space of the box could communicate with the working room.

An external view and a diagram of a two-section manipulator box intended for premises with a three-zone layout

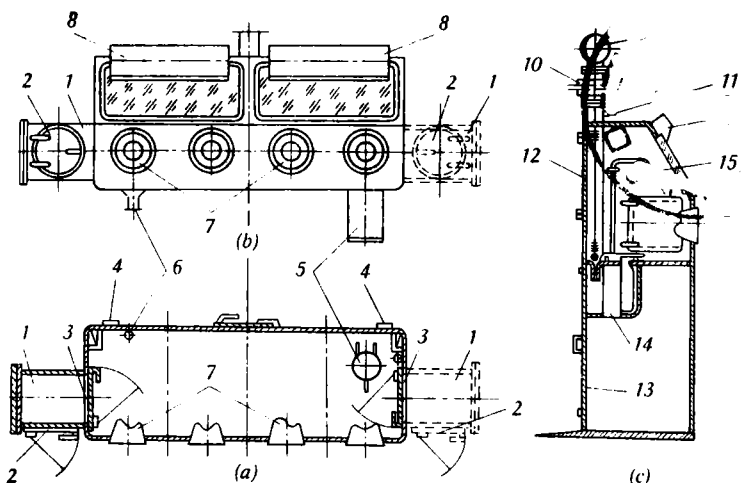


Fig. 0.5. Diagram of metal manipulator box with two work-places:

a—top view; b—view from side of operator's workplace; c—side view; 1—prechambers; 2—loading openings; 3—openings for connection of prechamber; 4—intake filters; 5—hatch for discarding solid waste; 6—drain to sewerage; 7—openings for gloves; 8—lamps; 9—ventilation duct; 10—filter; 11—handle of gate; 12—assembly opening; 13—gas protected door; 14—collector for solid waste; 15—shower on flexible hose

are shown in Figs. 0.4 and 0.5. The assembly doors are on the rear wall opening into a different room, access to which is possible only through a special sanitary lock.

Laboratory tables are made from materials readily lending themselves to cleaning: stainless steel, or metal coated with plastics. The table surfaces are finished in light colours with chemically stable, easily cleaned paint; the working surface is covered with a plastic or glass (Fig. 0.6). Work on such a table is performed in trays made from stainless steel, plastics, or enameled. All the utensils and appliances containing radioactive substances are placed in such trays.

Tables are designed to withstand an increased load, allowing shielding screens to be installed. A table is provided with all required supply inlets and drains. The cocks and switches of the communications are installed externally along the free side of the table.

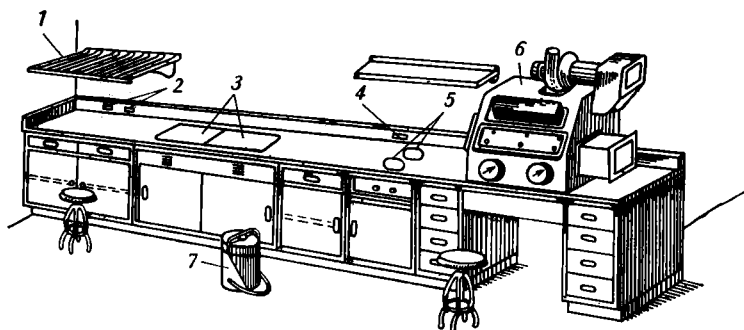


Fig. 0.6.

Laboratory table:

1—rack for drying utensils; 2—supply of air and gas; 3—sink with two compartments; 4—supply of electricity; 5—electric stoves; 6—glove box; 7—container for collecting solid waste

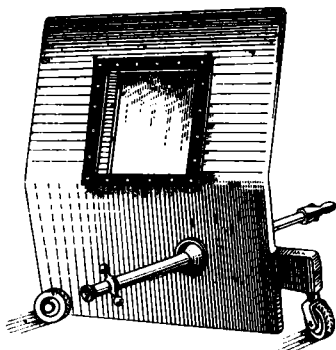


Fig. 0.7.

Movable shielding screen with lead glass window

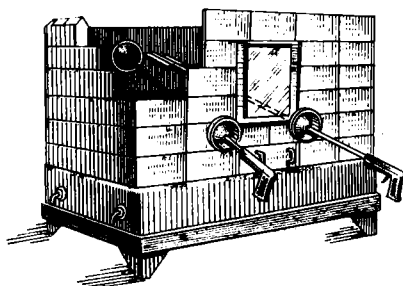


Fig. 0.8.

Sectional shielding screen of lead bricks with sword manipulators for work with γ -emitters

Shielding screens (their material, design, and thickness) are determined by the kind and energy of radiation of the radioactive isotopes used, the duration of work, and the nature of the performed operations. Screens may be stationary, movable, and sectional (Figs. 0.7 and 0.8).

For work with β -emitters, the shielding screens are made from glass (silicate or organic) from 8 to 10 mm thick. For work with γ -active substances, the screens are made

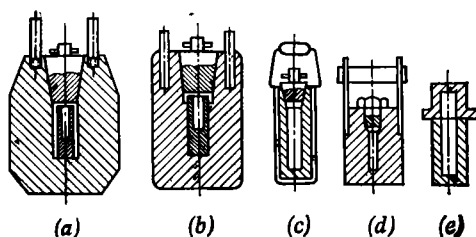


Fig. 0.9. Shielding transportation containers:
a, b, c—lead; d—steel; e—duralumin

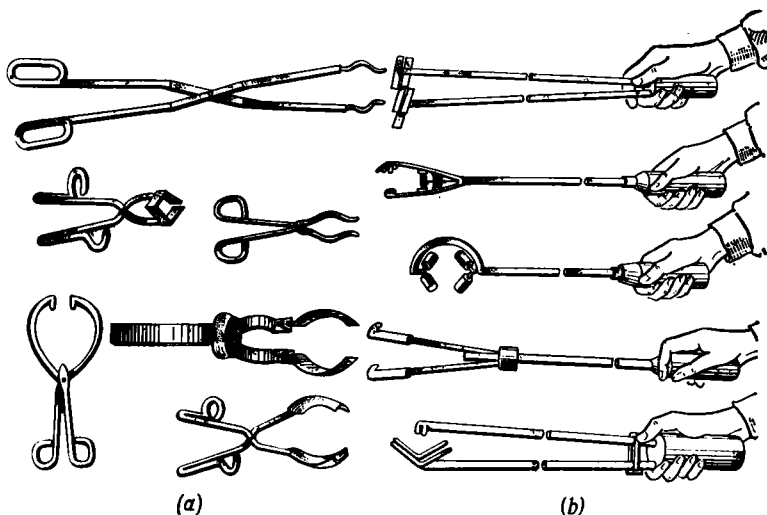


Fig. 0.10. A set of tongs (a) and grips (b)

from iron or lead with an inspection window of lead glass. Sectional shielding screens are made from shaped lead or iron blocks—bricks.

Containers (Fig. 0.9) are shielding vessels specially intended for the transportation and storage of radioactive substances. The type of container, its material and wall thickness are determined by the amount of a radioactive isotope to be held in it and the nature of its radiation. For γ -emitting

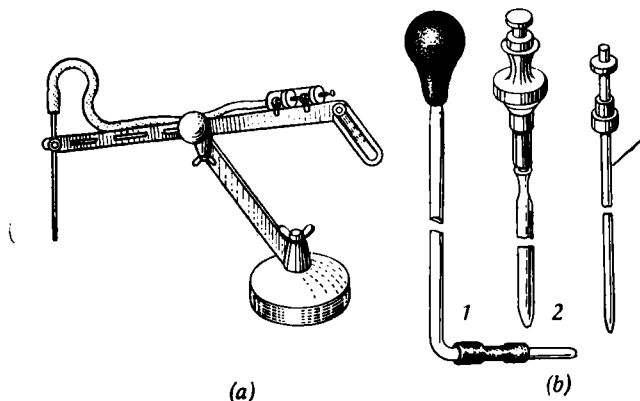


Fig. 0.11. Means for sampling liquids:
a—remote-control pipette; *b*—various kinds of pipettes;
 1—with a rubber bulb; 2, 3—with a piston pump

substances, containers are made from lead or iron with massive walls. Aluminium and Carbolite (a phenol-formaldehyde resin) containers are used for storing β - and α -active isotopes. For sources of neutrons, containers with double walls of sheet steel, the space between which is filled with paraffin and boron carbide, are employed.

Remotely controlled contrivances (manipulators and mechanisms) are intended for working with radioactive substances at a distance.

Manual manipulators are distinguished by their great variety, and each of them is intended for performing one or more simple operations. Various kinds of tongs and grips (Fig. 0.10) are very simple manipulators. A set of grips usually consists of three handles of different shapes (350, 600, and 850 mm long) with interchangeable grips for test tubes, beakers, cups, flasks; the grip jaws correspond to the shape of the object to be handled.

Samples of a radioactive liquid are taken in a laboratory with the aid of a medical syringe connected to a pipette by means of a flexible rubber tube. Liquids with a high activity are sampled with the aid of remotely controlled means such as a remote control pipette (Fig. 0.11*a*) that allows one to perform the dosed sampling and pouring over of a liquid. Liquids can also be sampled with the aid of a pi-

pette with a rubber bulb, or controllable automatic pipettes and micropumps (Fig. 0.11b).

The utensils used for work with radioactive substances may be of the kind usually employed in chemistry, but they must be of a better quality—especially resistant to heating, to the action of chemical reagents, and must have an increased mechanical strength. If experiments are being run with solutions of a low concentration, it is good to use utensils made from Teflon (polytetrafluoroethylene), quartz, and other materials adsorbing radioactive substances to a smaller extent than glass.

MEASURES FOR INDIVIDUAL PROTECTION AND HYGIENE

When working with bare radioactive isotopes, contamination of the outer surfaces of the equipment, appliances, overalls, individual means of protection, and skin of the workers is possible. The level of the contamination must never exceed the values given in Table 0.6.

Table 0.6. Permissible Contamination by Radioactive Substances, cpm/cm²

Contaminated object	α -Emitters		β -Emitters
	highly toxic (APC = 2×10^{-15} Ci/li-tre)	miscellaneous	
Skin	5	5	100
Towels	5	5	100
Main overalls (smock)	10	40	800
Gloves	10	40	2000
Additional overalls:			
(a) inner surface	10	40	800
(b) outer surface	100	400	8000
Surfaces of working premises of zone being controlled	10	40	2000

No contamination of personal belongings and clothing with radioactive isotopes is tolerated. If this does happen, personal clothing and footwear must be deactivated to the

level of the natural background. Should deactivation be impossible, they must be buried like radioactive waste.

All persons working with bare radioactive substances must be furnished with individual means of protection depending on the kind and class of their work.

MEANS FOR INDIVIDUAL PROTECTION

Overalls are articles made from fabric, plasticized substances, and other materials intended for protection of the entire body or separate parts thereof from contamination when working with radioactive substances.

When there is a hazard of even insignificant contamination, all work with radioactive isotopes must be performed in overalls and caps made from an undyed fabric (coarse calico, satin, moleskin, polyethylene terephthalate) because dyes usually detract from the desorption properties of fabrics. Overalls made from fabrics do not always ensure reliable protection of the body's surface. When there is a danger of substantial contamination, one must put on film clothing over the fabric one—oversleeves, aprons, robes, pneumatic suits. Film clothing ensures more complete protection of the body's surface against radioactive substances and dust getting on it, and also against acids and alkalis that may be used when working with radioactive substances.

The hands are protected with **gloves** when working with radioactive substances. Thin surgical, rubber, isoprene, or vinyl chloride gloves are used.

One must know how to properly use gloves, put them on and take them off. The cleanliness of one's hands and safe work with radioactive isotopes depends on this. When putting on gloves, one must take hold of the inner side of the cuff (Fig. 0.12) with a bare hand, and only of its outer side with a hand in a glove. Before putting on gloves, powder your hands with talcum. After putting on both gloves, turn back the cuffs and adjust the gloves on your fingers. When putting gloves on or taking them off, see that their outer side never touches the inner one, and that your bare fingers never touch the outer side of the gloves. Take off gloves with the same care as when putting them on. First thoroughly wash the gloves when on your hands to remove radioactive contaminants from them, then dry

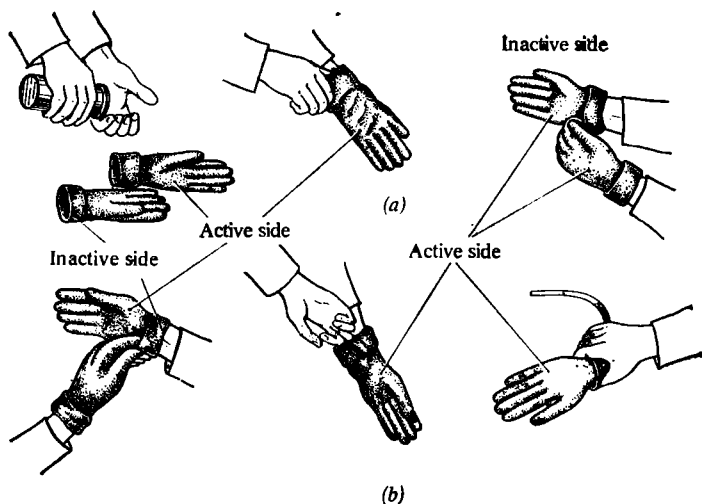


Fig. 0.12. Ways of putting on (a) and taking off (b) gloves

them and powder them with talcum. Fold the cuffs onto your wrists, insert your fingers in gloves into the fold, take off a glove, and return it to its normal state. Grip the second glove with your fingers inside, take it off, and return it to its normal state. Straighten out the gloves using compressed air, and powder them inside with talcum because otherwise they may stick together at moist spots, which will hamper their further use.

Store gloves wrapped up in fabric in a drawer of the table, or in special lockers fitted onto special bars. Periodically check the gloves and discard punctured or torn ones.

Special footwear is intended for protecting the feet from contamination by radioactive isotopes. When constantly working with radioactive substances, it is recommended to change one's own footwear in the laboratory to working footwear (usually slippers made from natural or artificial leather). Film boots (Fig. 0.13) are put on when considerable contamination is possible.

Protection of the eyes is an essential condition when working with radioactive isotopes.

To protect the eyes against external α - and β -radiation, goggles or masks with a transparent thermoplastic (Plexiglas) 2-5 mm thick are used.

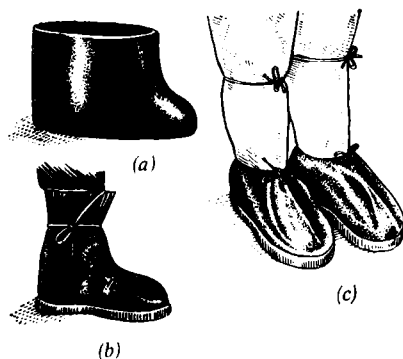


Fig. 0.13. Special footwear for working with radioactive substances:
a—rubber boots; *b* and *c*—boots of a plastic compound

It is desirable that the rim of the goggles be of the closed type and protect the eyes from radioactive dust or vapour getting into them.

The **respiratory organs are protected** with the aid of **respirators, gas masks, helmets, and pneumatic suits**. The greatest favour has been given to a respirator for one-time use (Fig. 0.14), in which the filtering material is fabric FP with a purifying efficiency of 99.9%. The respirator is put on beginning with the chin, next the aluminium plate is pressed against the nose to take its shape, and then the straps are tied and the edge of the respirator is smoothed against the skin of the face.

At a higher concentration of radioactive dust and aerosols, a respirator in the form of a helmet-mask is used. Isolating devices with oxygen cylinders or pneumatic suits provide more reliable protection than respirators.

Isolating devices are used when inert radioactive gases such as radon and xenon are present.

The main overalls and underclothes must be deactivated in special laundries. Additional plastic overalls, goggles, masks, gloves, etc. must be deactivated in specially assigned places.

It is prohibited to take out clean or dirty overalls for washing in ordinary laundries or in domestic conditions.

In connection with the danger of radioactive isotopes getting into an organism in premises where experiments

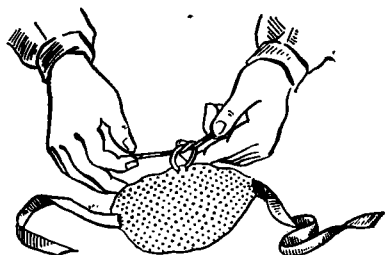


Fig. 0.14. Antidust respirator "Lepestok"

are being run with bare radioactive isotopes, it is strictly prohibited:

(a) to let workers be in the premises without the required individual means of protection;

(b) to store food products, tobacco, cigarettes, domestic clothing, cosmetics and other objects having no relation to the work in the premises;

(c) to take food, smoke, or use cosmetics.

A special room is provided for taking food and smoking. It is outfitted with a washing stand for washing one's hands with a supply of hot water and with a radiometric instrument for self-control. This room must be completely isolated from the premises where experiments with bare radioactive substances are being performed.

DECONTAMINATION

In performing experiments with bare sources of radioactive radiation, contamination of the utensils and appliances is inevitable, and it is also possible that the laboratory furniture, equipment, overalls, unprotected parts of the body, etc. will be contaminated.

The amount of a radioactive isotope retained on a surface depends on the nature of the material, the chemical state of the surface, and on the chemical state and state of aggregation of the radioactive isotope.

The processes leading to the retaining of radioactive isotopes on a surface can be divided into mechanical and chemical ones. Mechanical contamination in the pure form is encountered exceedingly rarely, and it is usually attended by various chemical processes. When a surface is contami-

nated with powders and solutions of radioactive substances, the strength with which these substances are retained depends on the roughness and porosity of the surface material, the dispersity of the radioactive powder, on various kinds of adsorption and electrochemical processes, and on the rate of bulk and surface diffusion of the radioactive substance. A radioactive substance may also enter into a reaction of isotope and ion exchange with the material of the surface.

The ion-exchange properties of a surface are due to the presence of free valence bonds or of active groups such as $-\text{OH}$, $-\text{COOH}$, and $-\text{NH}_2$. The adsorptivity of a surface depends greatly on its preliminary treatment, on the acidity and salt composition of a radioactive solution.

For example, the preliminary treatment of the surface of glass with an acid or alkali increases the adsorption of cations because of the formation of the active groups $-\text{SiO}-\text{H}$ with acid treatment and the groups $-\text{Si}-\text{OH}$ and $-\text{SiO}-\text{Me}-$ with alkali treatment. Many radioactive isotopes (especially those of the transition elements) are inclined to form colloidal solutions. In addition, pseudo-colloids may be formed of various radioactive isotopes of the elements which in macroamounts do not form colloidal solutions. The adsorption on a surface of ion exchangers when dealing with true solutions increases with an increase in the pH (the acidity diminishes); the adsorption of colloidal solutions depends on the degree of hydrolysis of a radioactive isotope.

The retaining of radioactive isotopes on metals usually has an intricate mechanism including electrochemical exchange (the evolution on a metal of cations of the elements that are lower in the electromotive series), isotope and ion exchange, and various adsorption processes.

In all cases of contamination with radioactive isotopes, it is necessary to establish the level of contamination, determine (if possible) the isotope contaminating the surface, and perform decontamination up to the levels indicated in Table 0.6. The contamination level is determined with radiometers whose scale must be graduated according to the radiation of radioactive isotopes having a spectral composition of their radiation close to that of the contaminated surface. The choice of decontaminants in each case must be individual and take the above factors into account.

Determination of the contamination levels and the qualitative composition of the radioactive contaminants is followed by decontamination. The desorption of radioactive isotopes forming true solutions is maximum at $\text{pH} = 1$. This underlies the use of acid decontaminating solutions. The desorption of isotopes inclined to form colloids depends on the acidity of the solution of the radioactive isotope at the instant of application to the surface and has a minimum in the region of pH's corresponding to the maximum adsorption.

As a rule, surfaces contaminated by radioactive isotopes in the colloidal state lend themselves with greater difficulty to decontamination. The latter in this case can be performed the most effectively by using appropriate complexing agents in an acidic or alkaline medium.

The rare-earth elements, niobium, tantalum, zirconium, and some other transition elements form stable complexes with citric and oxalic acids. Decontamination here is due to the formation of complex anions of the type $(\text{MeX}_2)^{3-}$ that are virtually not adsorbed by cation-exchange surfaces (here Me is a transition element cation, and X is an acid residue).

Surfaces contaminated by bi- or trivalent cations of radioactive isotopes (Sr, Ba, Pa, Fe, etc.) can be decontaminated by alkaline solutions of ethylene diamine tetraacetic acid (EDTA) or its sodium salt (Na-EDTA). Complexions (aminopolycarboxylic acids and their derivatives) form with these cations stable complex anions of the type $(\text{Me}^{\text{II}}\text{Y})^{2-}$, $(\text{Me}^{\text{III}}\text{Y})^-$, and $(\text{Me}^{\text{III}}\text{OHY})$, where Me^{II} and Me^{III} are bi- and trivalent cations, respectively, and Y is a complexon anion.

When the qualitative composition of radioactive contaminations is known, decontamination can be performed with the use of a carrier—a stable isotope of the same element. The high effectiveness of decontamination with a carrier is explained by isotope dilution on the contaminated surface and by isotope exchange reactions. Mechanical radioactive contaminants are removed by means of various kinds of surfactants and detergents.

When the level of contamination cannot be lowered to the maximum permissible values with the aid of decontaminating solutions, one must resort to mechanical removal of the contaminated layer of the surface. To facilitate decontam-

ination, the inner surfaces of fume cupboards and glove and manipulator boxes are made from stainless steel, the working surfaces of tables are covered with poorly sorbing grades of plastics, and plastic overalls are used.

Table 0.7. Decontaminants Used for Decontamination of the Skin, Equipment, and Working Surfaces

Decontaminating solution (aqueous)	Removed radioactive isotopes of elements
2% EDTA	Zr, Ce, La, Ba, Be, Fe, Ca, Ag
2% detergent	Zn, Sr, Co, Pu, U, and fission products
2% sodium bicarbonate	Bi, Mo, Te, U, P
2% detergent	Mn, Au, Ce, Zr, Po, La, and fission products
1% HCl	Ag, Tl
1% sodium hyposulphite	Ag, Bi, Cu, Hg, Po
2% detergent	
2% thiourea	

Notes. 1. For decontamination of the hands, special pastes are available on the market, or various combinations: paste + decontaminating solution + sorbent.

2. To decontaminate working surfaces and equipment, the concentration of the solutions may be increased 2-8 times and a 0.5% solution of sodium hexametaphosphate added to them.

Table 0.8. Decontamination of Individual Protection Means

Material to be decontaminated	Decontamination stage	Decontaminant
Cotton fabric	I	0.1% soda + 0.3% HMP *
	II	0.5% soda + 0.5% soap + 0.4% HMP (boiling)
Polyethylene terephthalate fabric	I	1% soda + 0.5% potassium permanganate + 0.3% OP-7 (not over 80 °C)
	II	0.5% oxalic acid + 0.3% OP-7 + 1% HCl (not over 80 °C)
Film materials and rubber	I	2% HCl + 0.4% HMP + 1% detergent

* HMP = sodium hexametaphosphate.

It is sometimes good to cover the working surfaces with readily soluble hydrophobic varnishes or paints. Decontamination of such surfaces consists in removing the varnish or paint surface finish with a solvent and is often more effective to do than decontamination by conventional procedures.

Tables 0.7 and 0.8 contain recommendations on the decontamination of the skin, overalls, and working surfaces.

The decontamination procedure is determined by special instructions for each kind of work with a radioactive isotope (see, for example, the model instructions for work with bare radioactive isotopes).

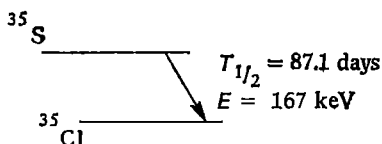
For performing work with radioactive isotopes, in each specific case instructions are drawn up at the place of work. Below are given model instructions for work with bare radioactive isotopes.

INSTRUCTIONS FOR WORK WITH RADIOACTIVE ISOTOPES IN LABORATORY (NAME OF LABORATORY)

COMPOUNDS LABELLED WITH ^{35}S

1. Basic Properties of Isotope ^{35}S

(a) Decay diagram



(b) Radiotoxicity group—C.

Maximum permissible activity at workplace:

class I $10^6 \mu\text{Ci}$

class II from 10^3 to $10^6 \mu\text{Ci}$

class III from 10 to $10^3 \mu\text{Ci}$

Maximum permissible activity at workplace not requiring permission of SES— $10 \mu\text{Ci}$.

(c) Effectiveness of registration when assaying with liquid^{*}organic scintillators—90%; when assaying with end-window counter SBT-7—10%.

(d) The critical organs for ^{35}S are the gonads, lungs, and gastrointestinal tract.

The mean annual maximum permissible concentration in the air of the working premises is 2.5×10^{-10} Ci/litre.

The flux density equivalent to the maximum permissible dose rate of external irradiation for the β -particles of ^{35}S is 16 cps/cm².

2. Maximum Permissible Levels of Contamination

Contaminated object	Permissible contamination according to rules OSP-72, cpm/cm ²	Counting rate	
		Liquid organic scintillator, cpm	SBT-7 (Luch-A), cps
Skin and inner side of gloves	100	90s *	0.5
Robe, main overalls	800	720s	3.5
Additional overalls:			
inner surface	800	720s	3.5
outer surface	8000	7200s	35
Working surfaces	8000	7200s	35

*s = area of taking smear (in cm²).

Notes: 1. Upon completion of work, the contamination of the hands must never exceed the background value.

2. No contamination of personal clothing, notebooks, and books is tolerated.

3. Protection from External Irradiation

Complete protection from β -radiation is ensured by screening the radiation source with a layer completely absorbing β -particles.

The maximum path of β -particles of ^{35}S is:

in air—30 cm

in water—0.35 mm

in glass—0.14 mm

The contribution of the braking radiation (bremsstrahlung) to the dose rate up to activities of 10 mCi may be disregarded.

4. Protection from Internal Irradiation

(a) The use of regular protective clothing (overalls, cap, slippers, gloves) when performing simple operations.

(b) The use of glove boxes and fume cupboards when performing complicated chemical operations.

(c) The use of additional means for protection (respirator, plastic overalls) when performing emergency work and decontamination of the glove boxes.

Caution! Remember that organic compounds of sulphur may penetrate into your organism through your gloves and skin. Regularly monitor the contamination of your hands, clothing, and gloves.

5. Nature of Operations to Be Performed and Conditions of Running Experiments

Operation	Classification of operations	Maximum activity at workplace, μCi	Class of work	Conditions of running experiment
Weighing dry substances	Simple	10^5	II	In closed vessel, in gloves
Repacking of dry substances and their dissolving	Complicated	10^3	II	In sealed glove box in closing vessel. Checking of contamination of outer side of container (smear)
Preparation of solution with preset specific activity	Simple	10^5	II	On tray, in gloves and mask
Boiling of solutions	Complicated	10^3	II	In fume cupboard. Vessel with reflux condenser. Monitoring atmospheric contamination. Gloves
Preparation of substances for measuring	Complicated	0.1	II	In fume cupboard under infrared lamp. Gloves
Measuring of substances	Simple	0.1	III	In measuring room without gloves. Pincers

Notes: 1. All the work is done consecutively. Upon completion of a stage of work, the workplace is decontaminated to permissible levels.

2. The utensils and other equipment must be marked (the isotope and maximum level of activity), for example, $^{35}\text{S} - 10^3 \mu\text{Ci}$.

6. Elimination of Accident

(a) An emergency situation appears:

when the maximum permissible contamination of surfaces is exceeded;

when the irradiation dose rate is exceeded;

when the APC is exceeded in the air;

in situations that may lead to contamination of the environment (a fire, flood, demolition of buildings, etc.).

- (b) Prediction of possible emergency situations:
decomposition of thiourea or barium sulphide (or their derivatives) chemically or thermally leading to gaseous decomposition products getting into the air of the working room;
spraying of a radioactive powder;
explosion of a reaction vessel in a glove box with the ejection of radioactive aerosols and gases through leaky spots;
fire in a fume cupboard or a glove or manipulator box;
spilling of a radioactive liquid.

(c) Information procedure:

The worker or his mate must immediately report the occurrence to the instructor. The latter must immediately report the accident to the administration of the laboratory and the radiation safety service (RSS). A decision on what further information is needed is taken by the laboratory administration and the RSS if the accident resulted in no injuries. If the accident resulted in injuries (including excessive irradiation), investigation and information are carried out in the usual way.

(d) Behaviour of personnel upon an accident:

1. The senior person in the premises determines the possible consequences of the accident and the injuries to the personnel (an appraisal).

2. Persons not occupied in elimination of the accident must switch off working installations, leave the premises (contaminated zone) after preliminary radiometric monitoring, and await the arrival of RSS inspectors in safe conditions.

Caution! Exit from a monitored zone of a laboratory after an accident is allowed only after a checkup by the RSS.

3. The senior person in the premises together with employees appointed by him take measures to eliminate the accident and guard the place of its occurrence; they report the accident to the instructor.

4. Should the air be contaminated with aerosols or radioactive gases, everyone must leave the premises after closing the windows and doors and switching on the ventilation.

(e) Measures for eliminating an accident:

Caution! Accidents are eliminated only with permission of the senior person in the premises or of RSS representatives.

1. Localize the place of the accident.

2. Check the contamination of the overalls, hands, and body. If the maximum permissible levels of contamination are exceeded, the overalls must be changed, and the hands and body decontaminated.

3. An accident may be eliminated only by persons having means of additional individual protection.

4. When extinguishing a fire, put on a gas mask or respirator.

Radioactive Liquids. Gather the liquid with a sorbing material (paper, waste, sawdust) into a special vessel. Wash the contaminated surface with a decontaminating solution. Do this downward and from clean sections to contaminated ones. In decontamination, perform radiometric monitoring of the washed and contaminated sections.

Use the following as a decontaminating solution: ethanol or acetone; a 10% solution of a detergent in water; water.

Radioactive Powder. Gather the powder with wads wetted in mineral oil. Perform final decontamination with alcohol, a solution of a detergent in water. Perform radiometric monitoring.

Notes: 1. When a stable fixed contamination is produced that does not lend itself to decontamination by conventional methods, it is permitted to remove a part of the contaminated surface (by agreement with the supervisor of the decontamination work).

2. All the materials used in decontamination must be accounted for as radioactive waste.

3. Participation in emergency work is entered in the personal card of dosimetric control of the relevant employee.

For information:

Telephones: Instructor _____
Head of laboratory _____
Radiation Safety Service _____
First aid _____
Fire department _____

Signatures: Head of department (laboratory)* _____
Instructor _____
Instructions compiled by _____

, 19 .

* When performing practical work, the instructions are signed by the instructor.

CONDUCTING PRACTICAL EXERCISES WITH THE USE OF BARE RADIOACTIVE ISOTOPES

1. Before beginning exercises in practical radiochemistry, the student must master the material of the introduction, the local instructions on practical work, and pass an examination on the safety rules when working with radioactive isotopes. The passing of this examination is entered in the record book of instruction in the safety rules.

2. The student draws up a plan of running an experiment, indicating the isotopes to be used, containing a calculation of the activity needed for doing the work, the activity level at the workplace, and indicating the forthcoming physico-chemical operations, the class of the work, and the proposed protective measures. He also draws up instructions for performing the given experiment.

3. All the details of the forthcoming experiment are reproduced in a "cold" experiment (without radioactive isotopes), and the separate stages of performing the work are clarified.

4. The instructor checks the presence of the required equipment for performing the work, the means of protection and eliminating accidents, the instructions for work with the given isotope and gives permission for obtaining the required radioactive isotope at the workplace.

5. The laboratory technician upon receiving an order signed by the instructor issues the ordered radioactive isotope in the appropriate packing.

6. The student enters in his working record intended only for practical work in radiochemistry the initial data of the obtained isotope (its activity, specific activity, volume, mass, radiochemical purity, chemical compound, physical state). Subsequently, all operations with the radioactive isotope are entered in the record.

7. It is prohibited to take a working record out of the working room. If necessary, the data obtained may be copied into another, "clean" record in a special room intended for processing the results of a radiochemical experiment.

8. Upon completion of work, the student hands in the unused radioactive isotopes, radioactive preparations, and radioactive waste to the laboratory technician.

It is prohibited to take any radioactive preparations out of the laboratory.

9. The student performs a radiometric survey under the control of the laboratory technician or radiation supervisor and when necessary decontaminates his workplace, utensils, and other equipment, and again hands in the radioactive waste.

10. The laboratory technician or radiation supervisor monitors the level of contamination of the overalls, personal belongings, and skin of the student. If the established standards are exceeded, decontamination is performed.

11. A student may leave the laboratory only with the instructor's permission after a dosimetric survey.

INTRODUCTORY WORK.

PREPARING A SOLUTION WITH A PRESET ACTIVITY

Before performing chemical work with radioactive substances, one must learn how to prepare their solutions with a preset specific and general activity, and also acquaint

oneself with the procedures for making preparations for activity measurements.

A. REQUIREMENTS TO SOURCES FOR MEASURING RADIOACTIVITY

Relative measurements consist in comparing the rates of counting for two or more preparations (sources) containing identical isotopes. The change in the registered counting rate I allows one to appraise the course of the process being studied because the quantity I is proportional to the absolute activity A , i.e. $I = \varphi A$, where φ is the counting coefficient. It includes all the corrections appearing when radiation is measured. Consequently, for the proper performance of relative measurements, it is necessary to ensure reproducible conditions for preparing and measuring sources of one series. This signifies that, for example, solid sources of a series must have a mount or backing from the same material of equal thickness; an active layer identical in area, shape, and thickness; uniform or reproducible distribution of the substance. Prior to measurement, all sources must be thoroughly dried and arranged identically relative to the counter in a holder of the same shape. A single installation with the same counter must be used in the measurements.

The requirements which sources emitting α -, β -particles, or γ -quanta must meet differ somewhat. For example, α -sources of one series may be prepared on backings with a different atomic number because the effect of α -particle scattering from the backing may be ignored. Sources emitting low-energy β -particles must meet high requirements as regards the thickness of the active layer and the uniformity of distribution of the substance over its mount. In these cases, however, it is considerably simpler to prepare sources with a thickness of the active layer exceeding the maximum path of the β -particles of the given isotope. For γ -quanta, the material of the backing, its thickness, and the thickness of the layer of radioactive substance may vary somewhat because the effects of absorption and reflection of γ -quanta are low and are not taken into account in conventional measurements.

In absolute measurements of the activity, the registered counting rate equals the absolute activity: $I = A$. This

points to the need of preparing sources that do not require the introduction of any corrections. Sources will meet this requirement if, first, the radioactive substance is distributed over the area of the active spot in a very thin layer, and, second, if the mount of the source is sufficiently thin and is made from a substance with a low atomic number. Notwithstanding the fact that the requirements to sources for absolute measurements are considerably higher than for relative measurements, methods have been developed that allow one to solve this problem successfully and obtain a thin film of radioactive substance distributed on a thin but strong organic film.]

The requirements which sources intended for relative or absolute measurements must meet, are taken into account when preparing sources by any method.

B. PROCEDURES FOR PREPARING SOURCES ON A MOUNT

Evaporation of Solution on a Mount

The mount may be made from any material such as filter paper, metal, glass, or organic substances; it may have the most diverse shape: disks, plates, cups, etc.

Procedure for Preparing Sources on Filter Paper. Cut a circle 3-4 cm in diameter out of filter paper and draw a circumference on it whose diameter equals that of the window in an end-window counter. Apply a solution of Plexiglas (transparent thermoplastic) in dichloroethane (1-1.5%) to the outer edge of the circle in the form of a ring several millimetres wide. This is usually done with a small-diameter glass tube or a thin brush. The filter is dried, and the ring transforms into a hydrophobic one. A ring is applied in a similar way to the other side of the filter.

Place the filter on an annular support so that the diameter of the latter exceeds that of the ring. To improve the distribution of the radioactive substance over the area of the active spot, first apply a small amount of a surfactant solution to the filter, for example, one or two drops of a 5% solution of insulin. Next use an ordinary or capillary pipette connected to a syringe to apply two or three drops of the radioactive solution onto the filter; see that the solu-

tion does not drop through the filter. Transfer the latter under a hood in a Petri dish or a small tray arranging the filter so that the wetted portion does not touch the bottom, for example on a latticed glass support. Evaporate the solvent under an infrared lamp, arranging the latter at a height of 10-15 cm from the source. Finally cover the active spot with a protective screen—a thin sticky tape or a thin organic film. In the latter case, apply 1-2 drops of a 0.5-1% solution of nitrocellulose in acetone per cm^2 of the active surface and dry it.

Procedure for Preparing Sources in a Plate. A solution with a low specific activity or with a small amount of the carrier may be prepared in a metal or glass plate (dish). Put the plate, whose diameter does not exceed that of the input window of the counter, at a distance of 10-12 cm from the tip of a pipette. Wet its bottom with 1-2 drops of a 5% insulin solution. Apply the aliquot of the solution without sharp ejection of the solution from the pipette; see that no air bubble forms on the tip of the pipette because this leads to a loss of activity. Evaporate the solvent under an infrared lamp, appraise the amount of carrier, and, if required, apply a protective organic film.

If a solution of a radioactive isotope contains sulphuric acid, bear in mind that only water is removed from such a solution upon its evaporation. The remaining hot and concentrated H_2SO_4 can readily react with a metal plate. This is why platinum is used as the backing material in such cases.

When a radioactive substance is dissolved in an organic solvent instead of in water, the sources for measuring radioactivity are prepared in bowls. If the organic solution contains appreciable amounts of nitric or hydrochloric acid, it is evaporated at a moderate temperature to avoid rapid decomposition of the solvent and its foaming because of violent evolution of vaporous and gaseous products.

It is convenient to prepare sources containing an α -emitter on metal disks. A hydrophobic ring, and then a solution of the radioactive substance are applied to degreased disks, for example from stainless steel, as described in the procedure for preparing a source on filter paper. After evaporation of the solvent and calcination, the source is ready for measurements.

Sources can also be prepared on thin organic films. The

procedure for doing this is similar to that for preparing a source on filter paper, except that the film is first pulled onto a thin metal or plastic ring.

Precipitation of Suspensions

This method of preparing sources is used when a radioactive substance is in the form of an insoluble compound. First a suspension in a suitable solvent is prepared from a precipitate, and it is then deposited onto a backing or mount by settling, filtration, or centrifuging.

Settling. The backing may be made from any material, but with a uniform and smooth surface. Simple devices are used to settle suspensions. A very simple device is shown in Fig. 0.15, in which the end of a glass tube is thoroughly ground in to the backing. A reliable connection can also be ensured by using an annular rubber gasket.

Procedure. Thoroughly grind the substance containing the radioactive isotope, the powder usually being wetted with an organic solvent. Transfer a weighed amount of the dried powder to a measuring cylinder or a test tube, add a sufficient amount of solvent, and stir the mixture. If a source with a comparatively thick layer of the radioactive substance is to be prepared, add a small amount of a binder to the solvent, for example a few drops of collodion, nitrocellulose varnish, or 20-30 mg of rosin per 100 ml of solvent. A thin active layer adheres well to the backing without the use of binders. Draw off a definite amount of the suspension and transfer it to the settling device with the preliminarily suspended backing arranged horizontally. See that the backing experiences no jolts, vibration, or other mechanical action. The device must never be moved during the settling process.

Settling may continue from several minutes to several hours and depends on the degree of dispersion of the precipitate, its amount, the volume of the solvent, the required thickness of the layer on the backing, and other factors. It is evident that only a part of the substance will settle during this time. Remove the solvent with the remaining substance by means of a pipette or siphon. Evaporate the solvent residues under an infrared lamp. Take apart the device, weigh the source, and after measurement of the area of the active layer, calculate its thickness. When

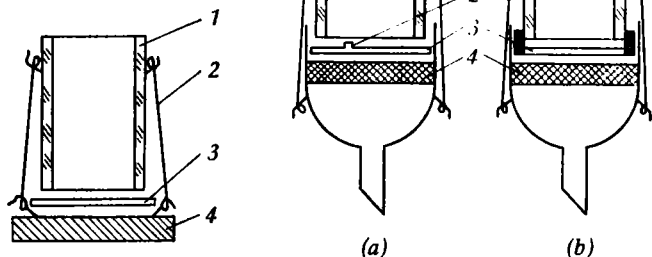


Fig. 0.15. A very simple device for settling a suspension:
1—glass tube; 2—rubber ring; 3—backing; 4—base

Fig. 0.16. Design of filtering units:
1—glass cylinder; 2—projection; 3—paper filter (a), paper filter with aluminium ring (b); 4—porous glass filter

doing this, disregard the presence of a binder in the layer. Cover the precipitate with a protective layer.

Filtration. The filtration of radioactive precipitates is performed with the aid of special filtering units. The design of some of them is shown schematically in Fig. 0.16. The main feature of these units is that porous glass plates (glass filters) are used in them for filtering the precipitate. Such devices make it possible to obtain layers of radioactive substances with a comparatively uniform thickness. Filter paper is mainly used as the backing.

Procedure. Cut out a filter whose diameter is somewhat larger than that of the glass cylinder (see Fig. 0.16). Leave a small projection at an arbitrary place of the filter onto which no precipitate will get when filtering; this is why the projection will be an original handle for extracting the source from the unit, its transfer, etc. Place the filter on a porous glass plate and wet it with one or two drops of water. Put the ground end of the glass cylinder on the moist filter and connect the Bunsen flask to a water jet pump. Wash the paper filter with several portions of water, and then with alcohol or acetone and ether. After doing this, dry the filter by letting air be sucked through it. Weigh the dry filter.

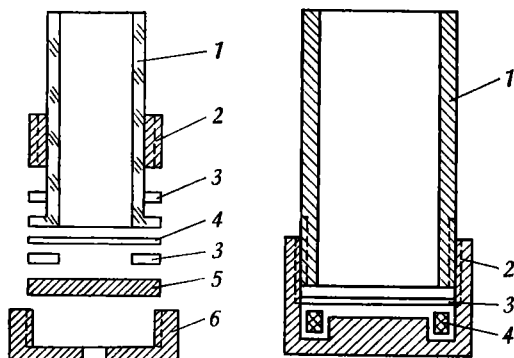


Fig. 0.17. Design of sectional test tube for centrifuging:
1—glass tube; 2—brass ring; 3—rubber gasket; 4—mount;
5—brass insert; 6—base

Fig. 0.18. Design of metal sectional test tube for centrifuging:
1—brass tube; 2—brass base; 3—mount; 4—rubber ring

Prepare a layer of satisfactory uniformity as follows. Before switching on the pump, fill the cylinder with a suspension about up to its half. In a few seconds, begin filtration at a moderate suction speed. Take care to see that the cylinder always contains a small amount of suspension. When filtration terminates, wash the precipitate with small portions of the solvent, and then let air be sucked through the precipitate for a few minutes to partly dry it. Extract the filter with the pump operating, carefully removing the glass cylinder. Extract the source from the unit with pincers, holding it by the projection or by the metal ring. Finally dry the precipitate under an infrared lamp and weigh it. Measure the area of the precipitate and calculate its thickness. Cover the precipitate with a protective layer.

Centrifuging. The suspension is separated from the mother liquor in special sectional (two-part) test tubes. The lower removable part of such tubes is a mount for preparing the source. Some very simple designs of sectional test tubes are shown schematically in Figs. 0.17 and 0.18.

Procedure. Prepare a suspension of the radioactive substance as indicated in the procedure for preparing a source by settling.

A definite volume of the suspension is transferred into the device for centrifuging with a preliminarily weighed

backing. The test tube is placed into a recess of the centrifuge, and the opposite arm of the latter is balanced. The speed and duration of rotation have to be established for each specific case. It must be remembered that in the conventional small laboratory centrifuges in conditions of the highest speeds of rotation, precipitates are formed, as a rule, that are not uniform in thickness. The optimal results are achieved at a moderate speed of rotation (2000-3000 rpm). After the completion of centrifuging, the solvent is carefully, so as not to damage the formed layer, removed with the aid of a pipette or siphon. The precipitate is washed when necessary. The residues of the solvent are evaporated under an infrared lamp. The device is taken apart, the source is extracted and weighed. The area of the precipitate is measured, and the thickness of the active layer of the source is calculated. A protective layer is applied.

Electrolytic Deposition

This method of preparing sources consists in that a radioactive isotope in a solution is deposited by an electric current on one of the electrodes playing the role of a backing. Deposition is performed in a cell that is included in the electric circuit together with instruments for measuring and controlling the current and voltage (Fig. 0.19). One of the simple designs of an electrolytic cell is similar to a device for precipitating a suspension by settling (see Fig. 0.15). It is evident that the radioactive isotope is deposited only on a backing of metal or of other materials with a metalized coating. In electrolysis, the isotope is customarily deposited on the cathode, therefore it is prepared in the form of a disk with a smooth surface. The anode can also be made in the form of a disk or wire (coil, ring). The formation of a uniform layer of the deposit is facilitated by good stirring of the solution during electrolysis, ensured by rotation of the anode. The speed of rotation does not exceed 100-200 rpm.

The electrolytic method is employed most frequently to prepare sources containing α -emitters (thorium, uranium, transuranium elements, etc.). They are highly electropositive elements, however, and at high values of the pH of the solution hydrolyze in the regions near the cathode and anode, forming precipitates of hydroxides or basic salts.

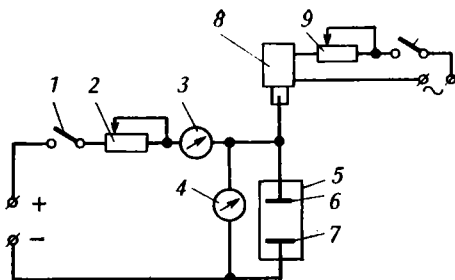


Fig. 0.19.

Electrical circuit of electrolyzer:

1—switch; 2—rheostat; 3—milliammeter; 4—millivoltmeter;
5—cell for electrolysis; 6—anode; 7—cathode; 8—motor for
rotating anode; 9—laboratory autotransformer

Such precipitates in the majority of cases adhere poorly to the backing electrode. The yield of the isotope is increased by performing electrolysis in an acid medium in the presence of complexing agents or with electrical deposition from aqueous and organic solutions. In these conditions, no hydroxide precipitates are formed, and the radioactive isotopes are deposited in the form of strong layers well adhering to the backing; the distribution of the substance over the area of such layers is highly uniform.

An example of employing electrolytic deposition for preparing a source is the procedure for depositing indicator amounts of the thorium isotope ^{230}Th from a water-ethanol solution onto a platinum cathode backing. A polished platinum disk is cleaned of impurities by boiling with an alkali, and is washed with nitric acid, distilled water, and ether. The anode in the form of a flat coil of platinum wire is placed 3-4 mm from the cathode. A cell is filled with 10 ml of a solution of ^{230}Th with an acidity close to neutral, and 2-3 ml of ethanol. Electrolysis is performed at a cathode current density of 180-220 mA/cm², a voltage of 3-4 V, and a temperature of the solution of 70-80 °C. In these conditions, 95-100% of the thorium is deposited during one hour on the cathode. Upon completion of electrolysis, the solution is removed from the cell, washed with a mixture of water and ethanol (1 : 1), the solvent residues are evaporated, the source is extracted, finally dried, and calcined.

Preparation of Thin Organic Mounts

Thin films of high-molecular organic substances are widely used as source mounts. Their thickness ranges from a few to scores of $\mu\text{g}/\text{cm}^2$. Skill is usually needed to prepare such a film. An important stage is measurement of the thickness of the obtained film. One of the best ways of measurement is by weighing.

Organic films conduct no electric current. This is why a source prepared on such a film may distort the electric field inside a counter or a counting chamber, which leads to a change in the counting rate in time. This effect is eliminated by applying to the surface of the film a thin layer of a substance capable of conducting an electric current (metallization of the film). The most widespread is metallization with gold or an alloy thereof with palladium; the coating thickness ranges from 1-2 to 15-20 $\mu\text{g}/\text{cm}^2$.

Procedure for preparing a collodion film about 0.1 μm thick. Dilute the collodion with an equal volume of amyl acetate. Rapidly apply two drops of this solution one after the other to the surface of distilled water in a vessel with a diameter of 25-30 cm. The liquid spreads over a circle with a diameter of about 20 cm and dries in a few seconds. A film about 0.1 μm thick forms on the surface. Submerge a wire frame in the water, bring it under the film, and lift it so that the film covers both sides of the frame. The need of forming a double layer is due to the fact that collodion films with a small thickness have a low mechanical strength. Dry the film. Next install it on a metal holder ring. For this purpose, coat the end of an aluminium ring having an outer diameter of about 20 mm with a thin layer of glue (for example, BF-2), carefully place it on the prepared film, which is on a glass plate, and hold it there a certain time for the glue to set. Lift the ring together with the film, and trim off its protruding portions.

Procedure for Preparing a Film from Polymethyl Methacrylate (PMMA). Pour 0.5-1.0 ml of a 0.5-1.0% solution of PMMA in dichloroethane onto a washed glass plate 8 $\times$ 8 cm in size and rapidly drain it off. Leave the plate in a horizontal position for about one hour at room temperature. Next place the plate with the film upward into a crystallizer with a small amount of water. After a certain time, the film will rise to the surface. If this does not occur,

trim off the edges of the film with a razor blade and carefully separate it from the glass. Put an aluminium ring under the film, extract it from the water, and dry it in the air. It is convenient to use PMMA films as mounts in preparing sources because they are hydrophobic, and an aqueous solution does not spread out over their surface.

It is good practice to apply a solution onto thin organic mounts with the aid of a micropipette.

C. PREPARING A SOLUTION WITH A PRESET RADIOACTIVITY

The atomic industry of the Soviet Union and other countries supplies radioactive isotopes of virtually all the elements of D. I. Mendeleev's Periodic Table. Radioactive isotopes are delivered in soldered glass ampoules, in ampoules with ground-glass stoppers, or in bottles hermetically closed with a rubber stopper and placed in lead or plastic containers. Each radioactive isotope is provided with a certificate indicating the chemical form of the element with the given radioactive isotope, the total and specific activity of the isotope at a definite time, and the mass of the chemical compound of the given element.

To prepare a solution of a radioactive isotope with the required total and specific activity (mass and volume) for an experiment, an approximate calculation is made, proceeding from the data in the certificate, of the amount of radioactive isotope that must be taken from the ampoule, the degree of its dilution, and of the amount of isotope carrier (a non-radioactive compound of the given element), which is taken in the same chemical form as the initial source. In the calculations, one must go over from the activity A expressed in Ci (mCi) to the activity in the units I on the instrument chosen for registration of the radiation (for a counter—cpm). Next, with a view to the conditions of measurement (the counting coefficient φ must be known or determined experimentally), the total activity is evaluated by the formula

$$I = \varphi A \quad (0.17)$$

and then the specific activity needed for the experiment is found using the expression

$$S_{\text{reg}} = \varphi S_{\text{abs}} \quad (0.18)$$

where S_{reg} and S_{abs} are the registered and absolute specific activities of the given radioactive isotope.

If the calculated total and specific activities needed for the experiment are less than the initial ones, all or a part of the total amount of isotope in the ampoule is used, and it is diluted with an isotope carrier.

Example. According to the certificate, we have an aqueous solution of Na_2HPO_4 containing ^{32}P that is in a bottle sealed with a rubber stopper. The total activity of the solution is 5 mCi, and its specific activity is 5 mCi/ml. The concentration of the phosphorus is 10 mg/ml.

Proceeding from the volume specific activity S_v , it is a simple matter for us to evaluate the specific activity per mole S_m :

$$S_m = \frac{S_v A_m}{c} = \frac{5 \times 31}{10 \times 10^{-3}} = 1.55 \times 10^4 \text{ mCi/mol} \quad (0.19)$$

where A_m is the atomic mass of the element (for phosphate $A_m = 31$); c is the concentration of the element containing the radioactive isotope (in our example $c = 10 \text{ mg/ml} = 10^{-2} \text{ g/ml}$).

It is necessary to prepare 5 ml of an aqueous solution of Na_2HPO_4 containing ^{32}P with a total activity of 10^5 cpm and a specific activity of 10^8 cpm/g of phosphorus.

The activity of the ^{32}P will be registered in a Geiger-Müller counter, the counting coefficient being $\varphi = 0.05$.

The total activity expressed in disintegrations per minute (dpm) is $A = 5 \times 3.7 \times 10^7 \times 60 = 1.1 \times 10^{10} \approx 10^{10} \text{ dpm}$, and $I = 5 \times 10^8 \text{ cpm}$.

Consequently, a dilution of

$$\frac{A\varphi}{10^5} = \frac{5 \times 10^8}{10^5} = 5 \times 10^3 \text{ times}$$

must be performed. It is difficult to perform such a large dilution directly, and therefore intermediate dilution is needed. We shall proceed as follows. We use a micropipette with a syringe to take 0.1 ml of the initial solution and put it in a measuring flask with a capacity of 50 ml. We add water up to the mark on the flask. Next we use a pipette with a syringe to take 2.5 ml from the solution and place it in a measuring flask with a capacity of 25 ml. With a view to the mass of the phosphorus introduced from the initial solution, we add a volume of the Na_2HPO_4 solution so that the total mass of the phosphorus in the entire flask will be 2.5 mg. Next we dilute the solution to 25 ml with water. We use a pipette with a syringe to transfer 5 ml from the 25-ml flask into an ampoule.

We thus prepare 5 ml of an Na_2HPO_4 solution containing ^{32}P with a total activity of $5 \times 10^5 \text{ cpm}$ and a specific activity of 10^8 cpm/g . The solution has a phosphorus concentration of 0.1 mg/ml or $(0.1 \times 10^{-3} \times 10^3)/31 = 3 \times 10^{-3} \text{ mol of P per litre}$.

To establish the exact value of the specific activity, we prepare a source of ^{32}P by precipitating it in the form of MgNH_4PO_4 . To do this, we take 0.1 ml of the solution, add a carrier (2 ml of a 0.05 M

solution of Na_2HPO_4), dilute it with water to 10 ml, and then add one drop of concentrated HCl and 10-12 ml of a solution of a magnesia mixture. Next, with continuous stirring, we introduce a diluted (1 : 1) solution of ammonia up to the noticeable formation of a precipitate. We add 10 ml more of ammonia (1 : 1) and let the precipitate stand for 20-30 min. We filter the precipitate through a paper filter on a funnel for preparing precipitates intended for measuring the activity. We measure the activity of the ^{32}P source using a Geiger-Müller counter with a counting coefficient of $\phi = 0.05$.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β - or γ -radiation. A funnel for preparing precipitates for measuring the activity. Glass bowls for measuring the activity. Two measuring flasks. Two 100-ml beakers. A micropipette. A pipette with a syringe for 1.5 and 10 ml.

Radioactive Substances. Compounds of ^{32}P , ^{131}I , ^{59}Fe , ^{60}Co , ^{89}Sr and others in ampoules, and certificates to them.

Reagents. Selected in accordance with the precipitation procedure.

Performance of Work

(a) Calculation of Required Dilution

Proceeding from the data in the certificate, the chosen method of measuring the radioactive isotope (the value of ϕ), and the task confronting you, calculate the amount of isotope needed for an experiment and the degree of dilution of the solution with a solvent and carrier.

(b) Opening of Sealed Ampoule and Preparation of Initial Solution

Put on gloves and the required overalls. Place the container with the ampoule behind the shielding screen. Extract the ampoule from the container with pincers or a grip (*never take hold of ampoules with your gloved hands!*) and secure it in a special holder. To open the ampoule, make a notch on its upper part with a cutter, and then put a wire heated by an electric current onto the place of cutting or touch this place with a red hot glass rod. Upon proper work, a uniform crack will form around the entire circumference of the ampoule, and it is easy to remove its top part.

Transfer all the contents of the ampoule (usually a solution) by means of a pipette into a test tube with a ground-glass stopper. If the radioactive isotope is supplied in the form of a solid substance, most often in a test tube with a ground-glass stopper, it is dissolved directly in the tube in a definite volume of solvent. Sometimes (if a part of the source is to be used), the solid radioactive substance is taken and placed in a new test tube with a ground-glass stopper, and is then dissolved.

Upon completion of the work, place the test tube with the radioactive solution closed with the ground-glass stopper in a container. Wash the pipette. Put the ampoule, solid and liquid radioactive residues into special collectors.

*(c) Preparation of Solution
with Preset Total and Specific Activity*

Put on gloves and place the container with the test tube on a tray behind a shielding screen (lead glass, lead bricks). Extract the test tube with the radioactive solution using a special grip, place it on the tray and secure it in a holder. Open the stopper with pincers. Put a second empty test tube with a ground-glass stopper on the tray and, if needed, a measuring flask of a definite volume. Take the calculated volume of solution from the first tube with a micropipette and put it into the second tube (sometimes intermediate dilution in a measuring flask is required). The walls of the pipette must be saturated with the radioactive solution (!). For this purpose, take the solution from the first tube into the pipette and force it back out.

Close the first tube with its stopper and remove it into the container. Introduce the calculated amount of the non-radioactive isotope of the given element in the same chemical form into the second tube with a pipette. Dilute the solution to the required volume. Close the second tube with its stopper and carefully stir its contents.

Wash the micropipette with the solvent, and then saturate its walls with the radioactive isotope by taking in and forcing out the solution in the second tube several times. Take two parallel samples (aliquot portions) from the test tube and prepare the sources in the chosen way.

Register the activity of these sources in the selected radiation detector. Calculate the total and specific activ-

ities of the prepared solution of the radioactive isotope on the basis of the measured activity of the sources, the amount of added mixture of non-radioactive isotopes, and the initial mass specific activity.

Compare the results of the experiment and calculations.

Remove the test tube into the relevant container. Wash all the utensils on the tray. Pour the liquid radioactive residues into a carboy, and put the solid ones into the collecting box.

Perform dosimetric monitoring of the utensils, workplace, and hands in rubber gloves.

PROCESSING THE RESULTS OF A RADIOCHEMICAL EXPERIMENT

The set of results obtained upon repeating experiments in identical conditions is customarily treated as a random sample from among an infinite hypothetical set including all the conceivable results that could be obtained in the given collection of conditions. This infinite hypothetical set is called a **population**, and samples taken from it, a **sample set**, or simply a **sample**. The results of experiments burdened by random errors are random quantities. The distribution of random quantities in a population is characterized by the values of its parameters — the **population mean** μ determining the location of the distribution centre on the numerical axis, and the **population variance** σ^2 that is a measure of the variance of a random quantity. The parameters of a sample including the results of n experiments $x_1, x_2, \dots, x_n$ are the **arithmetical mean (sample mean)**

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad (0.20)$$

and the **sample variance**

$$s^2 = \frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1} \quad (0.21)$$

The population parameters are constants whose exact values we do not know. The sample parameters are functions of the results of experiments (random quantities) and are

therefore themselves random quantities. The task of statistical treatment of data consists in appraising the parameters of the population according to sample data. For this purpose, we determine the boundaries of a numerical interval $(\bar{x} - \Delta_\gamma, \bar{x} + \Delta_\gamma)$ called the **confidence interval** within whose limits the value of the parameter being estimated may be found with a preset probability. The probability of the fact that the population parameter is within the interval confined between the values $\bar{x} \pm \Delta_\gamma$ is known as the **confidence coefficient** or **confidence level**. Customarily, a confidence level of 95% is set ($\gamma = 0.95$), although sometimes other values of γ are also used (for example, 0.90 or 0.99). The quantity $\pm \Delta_\gamma$ may be referred to as the **confidence error**, or the error corresponding to the confidence level γ .

To calculate the confidence errors, we must know the law which the distribution of the random quantity in question obeys. We usually assume that the results of experiments obey a **normal law of distribution** or a **Gaussian distribution**. In this case (when the population variance is not known), the error of the mean corresponding to the confidence level of γ is determined by the expression

$$\pm \Delta_\gamma = t_{\gamma, f} \frac{s}{\sqrt{n}} \quad (0.22)$$

where $t_{\gamma, f}$ is what is known as the Student coefficient whose value depends on the confidence level γ and the number of degrees of freedom $f = n - 1$ of the sample variance (see Appendix 4); s is the positive value of the square root of the sample variance (the **sample root-mean-square deviation**); and n is the number of experiments.

The lower limit of the error of a radiochemical experiment is determined by the error due to the statistical nature of radioactive decay. The distribution of the number of nuclei decaying in equal intervals of time that are small in comparison with the half-life (and of the number of counts registered by the detector in the absence of foreign sources of dispersion) obeys the **Poisson law**. For the Poisson law, we have $\sigma_p^2 = \mu$, therefore in the absence of errors violating the Poisson nature of the distribution (errors associated with the instability of the apparatus, the procedure followed in measuring the sources, the procedure of preparing them, etc.), the variance of the total number of counts N registered

by the detector during the time t must be

$$\sigma_{P(N)}^2 = \bar{N} \quad (0.23)$$

and the variance of the counting rate $I = N/t$ is

$$\sigma_{P(I)}^2 = \frac{\sigma_{P(N)}^2}{t^2} = \frac{\bar{N}}{t^2} = \frac{\bar{I}}{t} \approx \frac{I}{t} \quad (0.24)$$

In the presence of additional dispersion sources, the variance of the counting rate will no longer be determined by formula (0.24). This underlies the following method of testing the hypothesis of the Poisson nature of distribution of the results of measuring radioactivity. On the basis of n measurements of the counting rate each with a duration of t min, assuming that the Poisson distribution is observed, we calculate the experimental value

$$\chi_{\text{exp}}^2 = (n-1) \frac{s^2}{\sigma^2} = (n-1) \frac{s_I^2}{\bar{I}/t} \quad (0.25)$$

(where χ^2 is a random quantity); at a given number of degrees of freedom of the sample variance $f = n - 1$, there is a definite probability p of the fact that χ_{exp}^2 exceeds a certain limiting value χ_p^2 . In testing statistical hypotheses, this probability is called the **significance level**. The usual guideline for the significance level is 5% ($p = 0.05$). The values of $\chi_{0.05}^2$ depending on the number of degrees of freedom f are given in Appendix 5. If $\chi_{\text{exp}}^2 > \chi_{0.05}^2(f)$, then, since for the population variance calculated by formula (0.24) such an event has a low probability, we draw the conclusion that the hypothesis of the Poisson distribution of the results must be discarded. When $\chi_{\text{exp}}^2 \leq \chi_{0.05}^2(f)$, we assume that the distribution of the results may be considered to obey the Poisson law.

If the distribution of the results of measuring the radioactivity follows the Poisson law, the confidence error in the counting rate is evaluated by the formula

$$\pm \Delta_\gamma = u_\gamma \frac{\sigma_P}{\sqrt{n}} = u_\gamma \sqrt{\frac{\bar{I}}{nt}} \quad (0.26)$$

where u_γ is a coefficient whose value depends only on the confidence level γ ; to find the coefficient u_γ , one can use Appendix 4 because $u_\gamma = t_\gamma(\infty)$; nt is the total duration of the measurements.

In radioactivity measurements, the counting rate I_s of a source is obtained as the difference between the counting rate I_{s+b} of the source with the background and the counting rate I_b of the background. The confidence errors in the quantities I_{s+b} and I_b are determined directly by formulas (0.22) or (0.26), while the confidence error in the counting rate of the source $I_s = I_{s+b} - I_b$ is

$$\pm \Delta_\gamma(I_s) = \sqrt{\Delta_\gamma^2(I_{s+b}) + \Delta_\gamma^2(I_b)} \quad (0.27)$$

If dispersion is determined not by the statistical nature of radioactive decay, but by other reasons, and if the number of measurements of the source with the background and of the background is the same, i.e. $n_{s+b} = n_b = n$, and $f_{s+b} = f_b = f$, on the basis of expressions (0.22) and (0.27) we can write

$$\pm \Delta_\gamma(I_s) = t_{\gamma, f} \sqrt{\frac{s_{I_{s+b}}^2 + s_{I_b}^2}{n}} \quad (0.28)$$

When the dispersion of the results is determined only by the statistical nature of decay, the use of formulas (0.26) and (0.27) leads to the expression

$$\pm \Delta_\gamma(I_s) = u_\gamma \sqrt{\frac{\bar{I}_{s+b}}{n_{s+b} t_{s+b}} + \frac{\bar{I}_b}{n_b t_b}} \quad (0.29)$$

We can calculate *a priori* the duration of measuring the source with the background and the background alone needed for the error in the counting rate of the source due to the statistical nature of decay not to exceed the required level. If the value of δ_γ is set, i.e. the relative error in the counting rate of the source at a confidence level of γ associated only with the statistical nature of radioactive decay, the duration of measuring the source and the background t_{s+b} and only the background t_b should be:

$$\begin{aligned} t_{s+b} &= u_\gamma^2 \frac{I_{s+b} + \sqrt{I_{s+b} I_b}}{\delta_\gamma^2 I_s^2} \\ t_b &= u_\gamma^2 \frac{I_b + \sqrt{I_{s+b} I_b}}{\delta_\gamma^2 I_s^2} \end{aligned} \quad (0.30)$$

When choosing the optimal duration of measurements, it is convenient to use tables giving the total number of counts N that must be registered when measuring the source

with the background and only the background depending on the prescribed accuracy of the result and on the ratio of the counting rate of the source with the background to the counting rate of the background alone. Appendix 6 gives the values of N_{s+b} and N_b for various values of I_{s+b}/I_b and relative errors at a 95% confidence level. The duration of measurements is chosen with the aid of such tables as follows. The rate of counting the source with the background and only the background are preliminarily measured during one minute, and the ratio I_{s+b}/I_b is found. Next a table such as Appendix 6 is used to find the total number of counts when measuring the source with the background and only the background that must be registered at the prescribed level of the relative error. Dividing the tabulated total number of counts by the counting rate, we find the required duration of measurements. If the duration of measurements found in this way is long enough, it is good to divide it into several intervals of equal length. This division is useful for subsequent testing of the Poisson nature of distribution of the results.

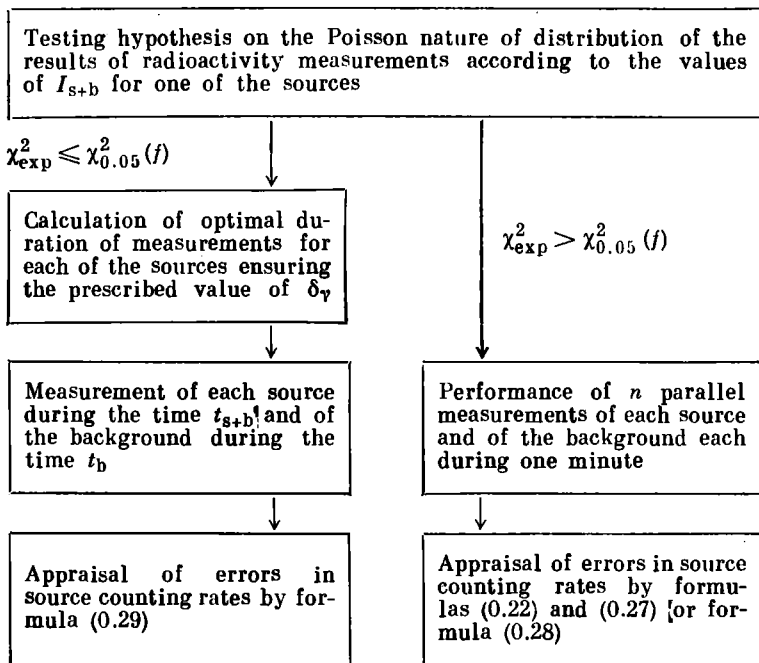
The sequence of operations in radioactivity measurements may differ depending on the conditions of running an experiment. We shall describe the two most typical situations.

1. A series of sources prepared in the same way at different stages of an experiment or in different experiments is measured. To test the hypothesis of the Poisson nature of distribution of the radioactivity measurement results, about 10 measurements of the counting rate (together with the background) are made of one of the sources, turning it each time through a random angle. If it is seen with the aid of the χ^2 -criterion that there are no grounds for rejecting the hypothesis on the Poisson distribution of the results, then for each source one calculates the optimal duration of measurements needed for the relative error δ_γ due to the statistical nature of the decay not to exceed the prescribed value at the confidence level of γ . Measurements of the activity being registered are performed during the required time, and the confidence errors of the counting rates of the sources are calculated by formula (0.29).

When the use of the χ^2 -criterion shows that the empirical distribution of the radioactivity measuring results differs appreciably from the Poisson distribution, there is no sense in finding the optimal duration of the measurements.

It is sufficient to perform several (the more, the better) measurements of each source and background each lasting one minute. It is natural that no further measurements are needed for the source used in testing the Poisson nature of distribution of the results because a sufficiently large sample of the values of I_{s+b} has been obtained for it. Next we evaluate the confidence errors of the source counting rates using formulas (0.22) and (0.27), or, if the number of measurements of the source and background and of the background alone is the same, formula (0.28). Diagram 1 shows the sequence of operations when performing radio-metric measurements in the case considered above.

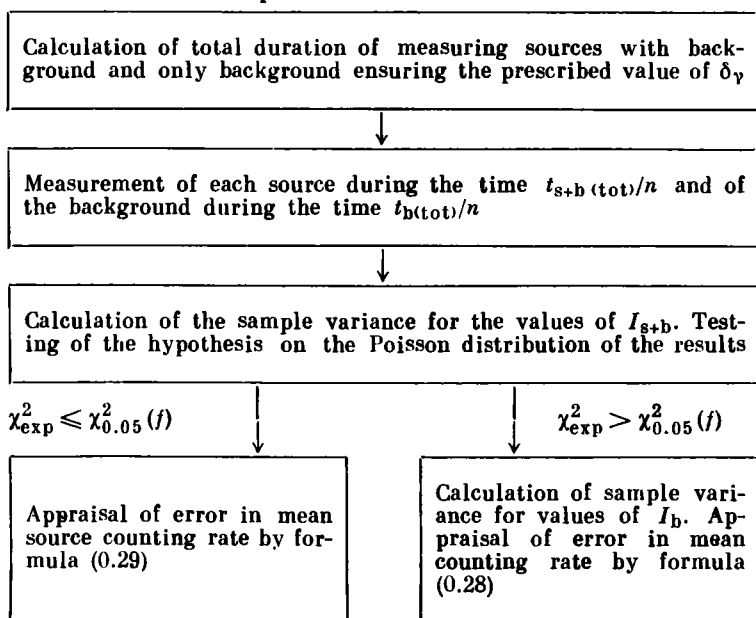
Diagram 1. Sequence of Operations When Measuring the Radioactivity of Sources Prepared in Different Experiments



2. A series of sources prepared in the same experiment is measured. Let all the sources be prepared in the same way from identical volumes of the radioactive solution (the

number n of parallel sources should be at least 3). One now proceeds as follows. Calculate the optimal total duration of measurements $t_{s+b(tot)}$ and $t_{b(tot)}$ at which the required value of the relative error associated with the statistical nature of decay (δ_γ) is ensured. Measure the registered activity of each source during the time $t_{s+b} = t_{s+b(tot)} / n$ and perform n measurements of the background each with a duration of $t_b = t_{b(tot)} / n$. Use the χ^2 -criterion to test whether the values of I_{s+b} follow the Poisson distribution. If there are no grounds to reject the hypothesis that the empirical distribution corresponds to the Poisson one, appraise the error in the result of measurements by formula (0.29). Otherwise use formula (0.28) to calculate the error. The sequence of operations described above is shown in Diagram 2.

Diagram 2. Sequence of Operations When Measuring the Radioactivity of a Series of n Sources Prepared in One Experiment



We must note that if the sources were prepared from different volumes of the radioactive solution or were mea-

sured in different conditions (different mounts, geometrical coefficients, etc.), it is impossible to test the hypothesis of the Poisson distribution of the results. In this case, all the results are reduced to the same volume of the solution or identical conditions of measurement, and the error is appraised by using formulas (0.22) and (0.27), or formula (0.28).

In performing a radiochemical experiment, it must be borne in mind that the systematic and random errors appearing at different stages of the work may substantially exceed both the errors due to the statistical nature of the decay and the total errors of radiometric measurements. Errors are possible which in experiments run in strictly identical conditions are systematic ones, and when the conditions of an experiment are varied are random ones. An objective appraisal of the accuracy and reliability of the data obtained can be found only as a result of repeating the entire experiment in several different conditions (for example, when determining the solubility, one should vary the duration of contact of the precipitate with the solution, the conditions of separation of the phases, the level of specific activity of the initial labelled compound, etc.). The results of parallel experiments are used to evaluate the arithmetic mean $\bar{x}$ and the variance s^2 and determine the error in the arithmetic mean at the prescribed confidence level [formulas (0.20)–(0.22)]. If parallel experiments are performed in the same conditions, it must be borne in mind that the appraisal of the accuracy obtained on the basis of these data will characterize only the minimum level of dispersion of the values of the quantity being studied.

When it is impossible to repeat an entire experiment from the beginning to the end, parallel measurements are performed at separate stages of the work, and the accuracy of the final result is appraised with the aid of the **law of error accumulation**. According to this law, the sample variance of the quantity Y , which is a function of k independent random quantities X_j

$$Y = g(X_1, X_2, \dots, X_k) \quad (0.31)$$

can be approximated by the expression

$$s_Y^2 = \left(\frac{\partial Y}{\partial X_1} \right)^2 s_{X_1}^2 + \left(\frac{\partial Y}{\partial X_2} \right)^2 s_{X_2}^2 + \dots + \left(\frac{\partial Y}{\partial X_k} \right)^2 s_{X_k}^2 \quad (0.32)$$

Here $s_{X_1}^2, s_{X_2}^2, \dots, s_{X_h}^2$ are the sample variances of the random quantities $X_1, X_2, \dots, X_h$.

Expression (0.32) continues to hold when we insert the squares of the confidence errors $\Delta_{Y(X_j)}^2$ into it instead of the variances. It is sometimes easier to find the relative characteristic of dispersion of the quantity Y directly. For example, the relative sample quadratic deviation of a function of several independent random quantities $w_Y = s_Y/Y$ is determined by the expression

$$w_Y^2 = \left[\frac{\partial}{\partial X_1} (\ln Y) \right]^2 s_{X_1}^2 + \left[\frac{\partial}{\partial X_2} (\ln Y) \right]^2 s_{X_2}^2 + \dots + \left[\frac{\partial}{\partial X_h} (\ln Y) \right]^2 s_{X_h}^2 \quad (0.33)$$

If we introduce the values of $\Delta_{Y(X_j)}^2$ into formula (0.33) instead of the variances, we obtain an expression for the relative error corresponding to the chosen confidence level δ_Y .

The error of the result of an experiment found with the aid of the law of error accumulation may be understated if certain sources of dispersion were not taken into account. Nevertheless, such an appraisal may be very helpful because it allows one to reveal the experimental operations that lead to the most substantial dispersion of the results. To lower the error in the result of an experiment, when performing these operations the number of parallel measurements should be increased, or the errors of an individual measurement should be lowered by improving the procedure of work. It is also good to use the law of error accumulation in the stage of the design of an experiment when one is to choose the procedure that will give the most accurate results.

In concluding, we shall consider a typical problem. It is necessary to determine the degree of isotope exchange F between the compounds AX and BX . In the general case, this quantity can be calculated, for instance, by the formula

$$F = \frac{S_{A,0} - S_{A,\infty}}{S_{A,0} - S_{A,\infty}} \quad (0.34)$$

where $S_{A,0}$, S_A , and $S_{A,\infty}$ are the initial specific radioactivity, the specific activity at the instant t , and the equilibrium specific activity of the substance AX , respectively.

Depending on the conditions of running the experiment, the error in the degree of exchange F can be appraised in

different ways. If the entire experiment from the beginning to the end was repeated several times and n values of F were obtained, by formula (0.21) we evaluate the variance characterizing the dispersion of the quantity F , and then by formula (0.22) find the confidence error of the mean $\Delta_{V(F)}$.

If in running the experiment, several parallel measurements of the quantities in formula (0.34) were performed, and the mean values of the specific activities were used to calculate the degree of exchange, the confidence error of the result should be calculated with the aid of the law of error accumulation. Let us use expression (0.32) to obtain a formula for appraising the error in the quantity F calculated from relation (0.34). First of all, we find the partial derivatives of the function (0.34) with respect to S_A , $S_{A,\infty}$, and $S_{A,0}$:

$$\begin{aligned}\frac{\partial F}{\partial S_A} &= \frac{1}{S_{A,\infty} - S_{A,0}} \\ \frac{\partial F}{\partial S_{A,\infty}} &= -\frac{S_A - S_{A,0}}{(S_{A,\infty} - S_{A,0})^2} \cdot 1 = -\frac{F}{S_{A,\infty} - S_{A,0}} \\ \frac{\partial F}{\partial S_{A,0}} &= \frac{(S_{A,\infty} - S_{A,0})(-1) - (S_A - S_{A,0})(-1)}{(S_{A,\infty} - S_{A,0})^2} \\ &= -\frac{1-F}{S_{A,\infty} - S_{A,0}}\end{aligned}$$

Substituting these derivatives into expression (0.32) and introducing $\Delta_{V(X_j)}^2$ instead of $s_{X_j}^2$, we obtain

$$\begin{aligned}\Delta_{V(F)}^2 &= \left(\frac{1}{S_{A,\infty} - S_{A,0}} \right)^2 \Delta_{V(S_A)}^2 + \left(-\frac{F}{S_{A,\infty} - S_{A,0}} \right)^2 \Delta_{V(S_{A,\infty})}^2 \\ &\quad + \left(-\frac{1-F}{S_{A,\infty} - S_{A,0}} \right)^2 \Delta_{V(S_{A,0})}^2\end{aligned}$$

Hence

$$\pm \Delta_{V(F)} = \frac{\sqrt{\Delta_{V(S_A)}^2 + F^2 \Delta_{V(S_{A,\infty})}^2 + (1-F)^2 \Delta_{V(S_{A,0})}^2}}{|S_{A,\infty} - S_{A,0}|} \quad (0.35)$$

where $\Delta_{V(S_A)}$, $\Delta_{V(S_{A,\infty})}$ and $\Delta_{V(S_{A,0})}$ are the confidence errors evaluated on the basis of parallel measurements of the corresponding specific activities.

If all the operations in determining the degree of isotope exchange were performed once, it is possible to appraise only the lower level of dispersion of the values of F deter-

mined only by the fluctuations of the measurement results associated with the statistical nature of radioactive decay [see formula (0.29)]. Assuming that at definite specific activities $S = I/V$ we may disregard the errors in sampling the volumes V of the solution, we have

$$\pm \Delta_{\gamma(S)} = \frac{1}{V} \Delta_{\gamma(I)} = \frac{u_{\gamma}}{V} \sqrt{\frac{I_{s+b}}{t_{s+b}} + \frac{I_b}{t_b}} \quad (0.36)$$

The confidence errors in the specific activities appraised in this way are introduced into (0.35), and the confidence error of the degree of isotope exchange is found.

Assume, for example, that the initial counting rate of the substance AX separated from 1.5 ml of solution was 2250 cpm; at the instant t , the counting rate of the substance AX separated from 1.6 ml of solution was 2100 cpm; when equilibrium distribution was achieved, the counting rate of the substance AX separated from 1.8 ml of solution was 1860 cpm (the counting rates are indicated without subtraction of the background). The background was 60 cpm, and the duration of all the measurements of the counting rates was 2 min each. Substituting into (0.34) the values of the specific activities $S_{A,0} = (2250-60)/1.5 = 1460$, $S_A = (2100-60)/1.6 = 1275$, and $S_{A,\infty} = (1860-60)/1.8 = 1000$ cpm/ml, we obtain

$$F = \frac{1275-1460}{1000-1460} = \frac{-185}{-460} = 0.402$$

The squares of the errors evaluated for the specific activities at a 95% confidence level ($u_{0.95} = 1.96$) in the given case are [see formula (0.36)]:

$$\Delta_{0.95(S_{A,0})}^2 = \left(\frac{1.96}{1.5}\right)^2 \left(\frac{2250}{2} + \frac{60}{2}\right) = 1972$$

$$\Delta_{0.95(S_A)}^2 = \left(\frac{1.96}{1.6}\right)^2 \left(\frac{2100}{2} + \frac{60}{2}\right) = 1621$$

$$\Delta_{0.95(S_{A,\infty})}^2 = \left(\frac{1.96}{1.8}\right)^2 \left(\frac{1860}{2} + \frac{60}{2}\right) = 1138$$

Introducing the corresponding values into expression (0.35), we find the confidence error of the quantity F :

$$\begin{aligned} \pm \Delta_{0.95(F)} &= \frac{\sqrt{1621 + 0.402^2 \times 1138 + (1 - 0.402)^2 \times 1972}}{|1000 - 1460|} \\ &= \frac{\sqrt{2510.40}}{460} = \frac{50.1}{460} = 0.109 \end{aligned}$$

Since the error is quite large, in writing the final result we can limit ourselves to two significant digits. Hence, the degree of isotope exchange is

$$F = 0.40 \pm 0.11 \quad (\gamma = 0.95)$$

* * *

Notice! Before beginning to perform an experiment, establish the class of the work according to the description on pp. 31-37. Give special attention to determining the class of work for individual operations.

Upon completion of an experiment, process the results as described on pp. 72-83.

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Part I General Radiochemistry

This part contains experiments in general radiochemistry dealing with the distribution of radioactive isotopes and elements between two liquid phases (extraction), a liquid and solid phases (coprecipitation, adsorption, ion exchange), and between two solid phases (isotope exchange).

When using these laws, one succeeds in separating and purifying radioactive isotopes and elements.

Chapter 1 Distribution of Radioactive Isotopes Between Two Liquid Phases

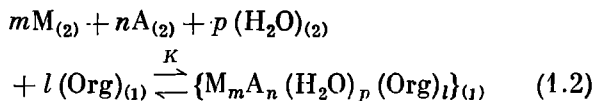
THEORETICAL INTRODUCTION [1-3]

According to the general principles of chemical thermodynamics, the distribution of any substance between two phases obeys the relation

$$\frac{a_{(1)}}{a_{(2)}} = \frac{\gamma_{(1)}c_{(1)}}{\gamma_{(2)}c_{(2)}} = K \quad (1.1)$$

where $a_{(1)}$ and $a_{(2)}$ are the thermodynamic activities of the substance in the first and second phases; $\gamma_{(1)}$ and $\gamma_{(2)}$ are the coefficients of thermodynamic activity (most often the molar and molal concentrations of the substance are used,

therefore $\gamma_{(1)}$ and $\gamma_{(2)}$ are the molar and molal coefficients of thermodynamic activity); $c_{(1)}$ and $c_{(2)}$ are the concentrations of the substance being distributed in the first and second phases*; and K is the equilibrium constant depending only on the temperature and pressure. Relation (1.1) also holds for describing extraction processes. It is more convenient, however, to consider the extraction of electrolytes as a chemical heterogeneous reaction. In the general case both water and the organic extracting agent (Org) are contained in the compound being extracted (hydration and solvation):



Neutral compounds (the charges on the cation and anion have been omitted) usually pass over into the organic phase. Quite often, solutions of the extracting agent in a suitable organic solvent (diluent) that does not react with the compound being extracted are used as the organic phase.

The equilibrium constant of reaction (1.2) is:

$$K = \frac{\gamma_{(1)} [M_m A_n (H_2O)_p (Org)_l]_{(1)}}{\gamma_{\pm}^{m+n} [M]_{(2)}^m [A]_{(2)}^n a_{H_2O}^p a_{Org}^l} \quad (1.3)$$

where a_{H_2O} is the thermodynamic activity of water in the aqueous phase, and a_{Org} is the thermodynamic activity of the extracting agent in the organic phase.

The organic substances used as extracting agents include oxygen-containing solvents (alcohols, ketones, ethers, and esters), amines and salts of quaternary ammonium bases, alkylphosphoric and carboxylic acids, and chelate-forming compounds. Saturated or aromatic hydrocarbons or their mixtures are used as diluents.

The following cases are encountered in the distribution (extraction) of an electrolyte between the aqueous and organic phases:

* Here and in the following, the subscripts (1) and (2) in parentheses indicate that the given substance (ion, etc.) is in the organic or aqueous phase, respectively. For example, $c_{(1)}$ and $a_{(1)}$ are the concentration and activity of a substance in the organic phase.

(a) a compound passes into the organic phase that does not dissociate in it;

(b) partial and more rarely complete dissociation of the compound being extracted occurs in the organic phase;

(c) partial or complete polymerization of the compound being extracted occurs in the organic phase.

When describing extraction equilibria, the distribution coefficient of the elements is ordinarily used. The **distribution coefficient** is defined to be the ratio of the total concentration of an element in the organic phase to its total concentration in the aqueous phase:

$$K_d = \frac{\sum_i [M]_{i(1)}}{\sum_j [M]_{j(2)}} \quad (1.4)$$

where $[M]_{i(1)}$ and $[M]_{j(2)}$ are the concentration of the element in all simple and complex forms in the organic and aqueous phases, respectively. If the cation M forms no complexes in the aqueous phase, and only the hydrato-solvate passes into the organic phase, (1.3) and (1.4) yield:

$$K_{d, M} = \frac{mK [M]_{(2)}^{m-1} \gamma_{\pm}^{m+n} [A]_{(2)}^n a_{H_2O}^p a_{Org}^l}{\gamma_{(1)}} \quad (1.5)$$

If complex ions of the element M with the anion A are formed, expression (1.5) should be divided by the sum

$\sum_{s=0}^K \beta_s [A]_{(2)}^s$, where β_s are the formation (stability) constants of the complex ions.

A growth in the concentration of a foreign salt (a salting out agent) usually increases the mean activity coefficient of the cation and the anion $\gamma_{\pm}$ in the aqueous phase, and as a result the distribution coefficient of the cation also increases (salting out). The addition to the aqueous phase of a salt having a common anion A with that of the compound being extracted increases the distribution coefficient of the cation both because of an increase in $\gamma_{\pm}$ and also simply as a result of an increase in the concentration of this anion. A growth in the total concentration of the salts in the aqueous phase is attended by a minor falling off of the activity of the water, but this decrease is completely compensated by the growth in $\gamma_{\pm}$.

Dilution of the extracting agent with an inert diluent, according to Eq. (1.5), lowers the distribution coefficient to $1/l$ of its initial value.

The extraction of macroquantities is attended by appreciable binding of the extracting agent in the organic phase, the result also being diminishing of $\gamma_{(1)}$. Here the value of the distribution coefficient decreases most frequently. And finally, upon the extraction of large amounts of a substance, for example $\text{UO}_2(\text{NO}_3)_2$, saturation is observed caused by the limited solubility of the compound being extracted in the organic phase. This phenomenon leads to falling off of the cation distribution coefficient with a growth in its concentration in the aqueous phase.

When the compound being extracted associates or dissociates in the organic phase, a dependence of an element's distribution coefficients on its concentration in the aqueous phase is observed even if $m = 1$:

(a) upon association

$$K_{d, \mathbf{M}} = \alpha + \beta [\mathbf{M}]_{(2)}^c \quad (1.6)$$

(b) upon dissociation

$$K_{d, \mathbf{M}} = \alpha + \frac{\beta}{\sqrt{[\mathbf{M}]_{(2)}}} \quad (1.7)$$

where α and β are quantities not depending on the concentration of the cation being extracted.

Upon the joint extraction of two or more substances, they mutually affect the distribution coefficients for a number of reasons. Of special significance for radiochemistry is the change in the distribution coefficients of microquantities of radioactive isotopes (elements) depending on the concentration of other substances in macroquantities. One of the causes of mutual influence in extraction is the competition of two or more substances in the formation of solvates (binding of the extracting agent). For example, binding of the extracting agent with large amounts of HNO_3 in extraction with tributylphosphate (TBP) of $\text{UO}_2(\text{NO}_3)_2$ and HNO_3 causes lowering of the uranium(VI) distribution coefficient.

Upon the dissociation of the compounds being extracted in the organic phase, there is also observed a decrease in the distribution coefficient of one cation (anion) with a growth in the concentration of the other cation (anion).

What occurs here is suppression of the extraction of microamounts of one element by macroamounts of another element if they are extracted into the organic phase in the form of salts with a common anion (cation) or in the form of simple or complex acids (the hydrogen ion is the common one).

When mixed compounds (associates) are formed in the organic phase, an increase in the distribution coefficient of one element is observed with a growth in the concentration of the other element in the aqueous phase. In the given case, coextraction of microamounts of the isotopes of one element with macroamounts of the other element occurs.

Now let us stop to consider the basic definitions that will be needed when performing practical work.

The extraction coefficient ε , the extracted fraction E , and the separation coefficient α characterize the effectiveness of the extraction method of separating and purifying substances.

For the extraction coefficient ε , we have:

$$\varepsilon = K_d \frac{V_1}{V_2} \quad (1.8)$$

where V_1 and V_2 are the volumes of the organic and aqueous phases.

The extracted fraction E with single extraction is

$$E = \frac{K_d}{K_d + (V_2/V_1)} \quad (1.9)$$

If $V_1 = V_2$, then

$$E = \frac{K_d}{K_d + 1} \quad (1.10)$$

In multifold extraction, the extracted fraction $E^{(n)}$ is evaluated by the formula

$$E^{(n)} = \frac{(\varepsilon + 1)^{n-1}}{(\varepsilon + 1)^n} \quad (1.11)$$

where n is the number of repeated extractions.

The separation coefficient α of two substances with distribution coefficients of $K_{d,I}$ and $K_{d,II}$ is

$$\alpha = \frac{K_{d,I}}{K_{d,II}} \quad (1.12)$$

It is quite evident that expression (1.12) corresponds to the actual state of affairs when there is no mutual influence of the substances being separated on the extraction.

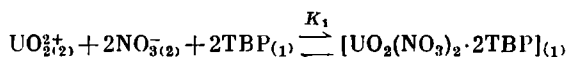
In the simplest case, extraction separation is performed in a separatory funnel or even in a test tube with a stopper. A variety of extractors is also available adapted for separating substances by single and multifold extraction.

Experiment 1.1. EXTRACTION OF $\text{UO}_2(\text{NO}_3)_2$ FROM AQUEOUS SOLUTION [1]

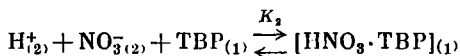
Uranyl nitrate is extracted well with solutions of tributyl phosphate (TBP) in kerosene. It is also extracted well with oxygen-containing solvents such as ethers and ketones. The distribution coefficient of uranyl grows noticeably in the presence of salting out agents.

A. EXTRACTION OF $\text{UO}_2(\text{NO}_3)_2$ WITH TRIBUTYL PHOSPHATE

Extraction follows the equation



Simultaneously, nitric acid is extracted, which binds part of the tributyl phosphate:



The concentration equilibrium constants are $K_1 \approx 6.0$ and $K_2 \approx 0.22$.

The coefficient of distribution of uranyl $K_d(\text{UO}_2^{2+})$ between the solutions of nitric acid and those of TBP in kerosene is evaluated by the following equation:

$$K_{d(\text{UO}_2^{2+})} = \frac{(c+A) \left[1 - \sqrt{1 - \left(\frac{c}{c+A} \right)^2} \right]}{2 [\text{UO}_2^{2+}]_{(2)}} \quad (1.13)$$

where c is the total molar concentration of the TBP in the organic phase equal to $c = (c_v \rho)/M$; c_v is the volume concentration of the TBP in kerosene, ml/litre; ρ is the density of the TBP equal to 0.973 g/ml; M is the mass of one mole

of TBP equal to 266.3 g; and A is a quantity determined by the following equation:

$$A = \frac{\{1 + K_2 [H^+]_{(2)} [NO_3^-]_{(2)}\}^2}{4K_1 [UO_2^{2+}]_{(2)} [NO_3^-]_{(2)}^2}$$

The object of the given experiment is to verify Eq. (1.13).

Equipment and Reagents

Equipment and Utensils. A shaker. Test tubes for 10 ml (15 tubes) for extraction with volume graduations and with ground-glass stoppers (the presence of graduations allows one to find the equilibrium volumes of the aqueous and organic phases). Conical flasks for titration. A micropipette for 0.2 ml. A burette for 25 ml. Pipettes with syringes for 1 and 5 ml. Bottles for 20-50 ml. Measuring cylinders for 10-50 ml. Measuring flasks for 25 ml (5) and for 50 ml (5).

Radioactive Substances. A 2 M and 0.5 M solution of $UO_2(NO_3)_2$.

Reagents. Tributyl phosphate. Kerosene. Solutions: 1.5, 10 M and concentrated— HNO_3 ; titrated 1.0, 0.1, and 0.001 M — Na_2CO_3 or $NaHCO_3$.

Performance of Work

Use the bottles to prepare mixtures (15-20 ml each) of uranyl nitrate and nitric acid of the following composition*:

- (1) 0.05 M $UO_2(NO_3)_2$ in 0.5 M HNO_3 ;
- (2) 0.05 M $UO_2(NO_3)_2$ in 1.0 M HNO_3 ;
- (3) 0.05 M $UO_2(NO_3)_2$ in 2.0 M HNO_3 ;
- (4) 0.1 M $UO_2(NO_3)_2$ in 0.5 M HNO_3 ;
- (5) 0.1 M $UO_2(NO_3)_2$ in 1.0 M HNO_3 ;
- (6) 0.1 M $UO_2(NO_3)_2$ in 2.0 M HNO_3 ;
- (7) 0.5 M $UO_2(NO_3)_2$ in 1.0 M HNO_3 ;
- (8) 0.5 M $UO_2(NO_3)_2$ in 2.0 M HNO_3 ;
- (9) 0.5 M $UO_2(NO_3)_2$ in 3.0 M HNO_3 ;
- (10) 2.0 M $UO_2(NO_3)_2$ in 3.0 M HNO_3 .

Prepare 5-7 ml each of 10, 20, 30, and 40% (by volume) solutions of TBP in kerosene.

Put 3 ml of the uranyl nitrate solution in nitric acid of the above concentrations into each of the test tubes for extraction. Add 3 ml of the chosen solution of TBP in ke-

* To prepare a solution, use the initial 2.0 and 0.5 M solutions of $UO_2(NO_3)_2$ and 1.5 and 10 M solutions of HNO_3 and water. Find the required volumes of the standard solutions for obtaining nitric acid solutions of $UO_2(NO_3)_2$ by calculation.

rosene to each tube. After mixing the phases in the test tube shaker during 3-5 minutes, determine the equilibrium volumes of the aqueous and organic phases according to the graduations. Next take 2-ml samples of the aqueous fraction from each tube using a pipette with a syringe and place them into other tubes. Determine the equilibrium concentration of the uranium in the aqueous phase after extraction in one of the ways described in experiment 10.2*.

Calculate the equilibrium concentration of the uranium in the organic phase, using in the calculations the initial and equilibrium concentrations of the uranium in the aqueous phase, and also the initial and equilibrium volumes of the aqueous and organic phases.

Evaluate the distribution coefficient K_d of the uranium by dividing the molar concentration of the uranium in the organic phase by the molar concentration of the uranium in the aqueous phase.

Use the micropipette to take 0.1-0.2-ml samples from the remaining aqueous phase and put them into conical flasks containing 20-30 ml of water. Determine the equilibrium concentration of the hydrogen ions in the aqueous phase by titrating these samples with a 1.0, 0.1, or 0.01 M solution of Na_2CO_3 or NaHCO_3 with methyl orange. Calculate the equilibrium concentration of the hydrogen ion and nitrate ion in the aqueous phase. Tabulate the results. Using the equilibrium concentrations of the uranyl, hydrogen, and nitrate ions in the aqueous phase and of the TBP in the organic phase, calculate according to formula (1.13) the coefficient of uranium distribution between the solutions of nitric acid at various concentrations of uranyl nitrate and the solutions of TBP in kerosene. Compare the experimental and calculated data and make conclusions on the applicability of Eq. (1.13).§

B. EXTRACTION OF $\text{UO}_2(\text{NO}_3)_2$ WITH DIETHYL ETHER

Here, depending on the composition of the aqueous phase, a compound containing a varying amount of water and ether passes into the organic phase (the hydrate and solvate num-

* If the amount of uranium in a sample is larger than that determined according to the chosen procedure, dilute the solution.

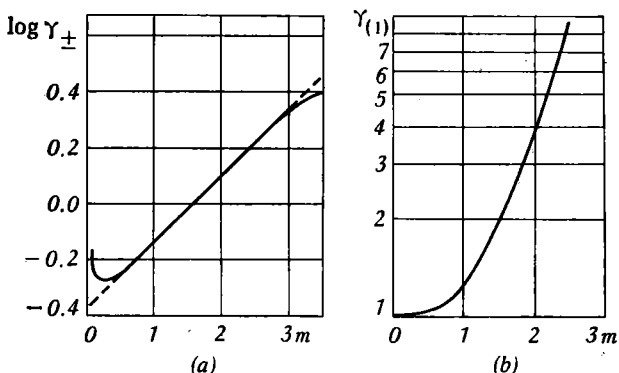
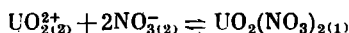


Fig. 1.1. Dependence of activity coefficients $\gamma_{\pm}$ and $\gamma_{(1)}$ of $\text{UO}_2(\text{NO}_3)_2$ on its molal concentration m (mol/1000 g of solvent) in an aqueous (a) and organic—diethyl ether (b) phases

bers are variable). In this connection, it is convenient to consider that the unhydrated and unsolvated salt $\text{UO}_2(\text{NO}_3)_2$ passes into the organic phase. The difference of the concentration of $\text{UO}_2(\text{NO}_3)_2$ in the organic phase from the thermodynamic activity, i.e. the non-ideal nature of the system, is taken into account by the thermodynamic activity coefficients. Hence, the extraction equation is written as follows:



The equilibrium constant K is

$$K = \frac{\gamma_{(1)}[\text{UO}_2(\text{NO}_3)_2]_{(1)}}{\gamma_{\pm}^3[\text{UO}_2^{2+}]_{(2)}[\text{NO}_3^-]_{(2)}^2} = \frac{\gamma_{(1)}[\text{UO}_2(\text{NO}_3)_2]_{(1)}}{\gamma_{\pm}^3 \cdot 4[\text{UO}_2^{2+}]_{(2)}^3} \quad (1.14)$$

i.e. the non-ideal nature of the system is taken into account by the thermodynamic activity coefficients $\gamma_{(1)}$ and $\gamma_{\pm}$.

The distribution coefficient of uranyl is

$$K_d = \frac{K\gamma_{\pm}^3 4[\text{UO}_2^{2+}]_{(2)}^3}{\gamma_{(1)}} = \frac{K\gamma_{\pm}^3 [\text{NO}_3^-]_{(2)}^2}{\gamma_{(1)}} \quad (1.15)$$

Figure 1.1 shows how the activity coefficient of uranyl nitrate in the aqueous and organic phases depends on its concentration in a solution.

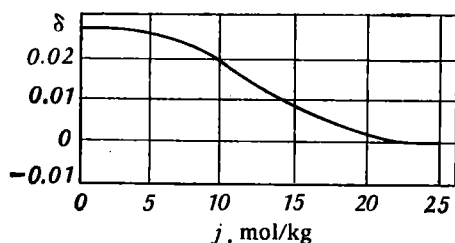


Fig. 1.2. Harned coefficient δ versus the ionic strength j of a solution when $\text{Ca}(\text{NO}_3)_2$ is used as a salting out agent

In the presence of salting out agents [for example, $\text{Ca}(\text{NO}_3)_2$], the theory of electrolyte mixtures has to be used to determine the activity coefficient of uranyl in the aqueous phase. According to this theory, we have

$$\log \gamma'_{\pm} - \log \gamma_{\pm} = 2\delta j \quad (1.16)$$

where $\gamma'_{\pm}$ is the thermodynamic activity coefficient of $\text{UO}_2(\text{NO}_3)_2$ in the presence of $\text{Ca}(\text{NO}_3)_2$ at an ionic strength of the solution equal to j , $\gamma_{\pm}$ is the thermodynamic activity coefficient of $\text{UO}_2(\text{NO}_3)_2$ without a salting out agent at the same ionic strength j , and δ is the Harned coefficient. Figure 1.2 shows δ versus j (in mol/kg) for $\text{Ca}(\text{NO}_3)_2$.

The distribution coefficient of uranyl nitrate in the presence of a salting out agent [see Eq. (1.15)] will be

$$K_d = \frac{(\gamma'_{\pm})^3 K [\text{NO}_3^-]_{(2)}^2}{\gamma_{(1)}} \quad (1.17)$$

The experiment is aimed at studying the applicability of Eqs. (1.15)-(1.17) for interpreting experimental data.

Equipment and Reagents

Equipment and Utensils. An analytical balance. A shaker. Test tubes for extraction with a scale of volumes (10). Pipettes with syringes for 0.1, 1.2, and 5 ml. Bottles for 20 ml (10). Weighing bottles (10).

Radioactive Substances. A 6.0 M solution of $\text{UO}_2(\text{NO}_3)_2$.

Reagents. Diethyl ether. A 4.0 M solution of $\text{Ca}(\text{NO}_3)_2$.

Performance of Work

Prepare 5-10 ml each of 1.0, 1.5, 2.0, 2.5, and 3.0 M aqueous solutions of $UO_2(NO_3)_2$ in the 20-ml bottles, and also 5-10 ml each of 2.0 M aqueous solutions of $UO_2(NO_3)_2$, but containing 2.0 and 2.5 mol/litre of $Ca(NO_3)_2$ *.

Put 5 ml of each of the aqueous solutions of uranyl nitrate of the above compositions into the test tubes for extraction. Also introduce 5 ml of diethyl ether into each tube. Extract the uranium by shaking for 5-10 min. Determine the equilibrium volumes of the aqueous and organic phases. Separate the aqueous phase, and, after taking out part of the solution, determine the equilibrium concentration of the uranium in the aqueous phase (use one of the procedures for determining uranium set out in experiment 10.2; see also the footnote on p. 91).

Knowing the initial concentration and volume, and also the equilibrium concentrations and volumes of the aqueous and organic solutions, calculate the concentration of uranyl nitrate in the organic phase. Determine the densities of the equilibrium aqueous and organic solutions by weighing 1 ml of each solution in each of the weighing bottles. Calculate the equilibrium molal concentrations of uranium (mol/1000 g) in the aqueous and organic phases. Determine the distribution coefficient of uranium (for at least two experimental results), and use Eq. (1.15) to calculate K . Depict the results graphically in the form of a dependence of the distribution coefficient of uranyl nitrate on its concentration in the aqueous phase and on the concentration of the calcium nitrate.

Using the values of the concentration of uranyl nitrate in the aqueous and organic phases, find the values of $\gamma_{\pm}$ and $\gamma_{(I)}$ from graphs (see Fig. 1.1), and by formula (1.15) calculate the distribution coefficient $K_{d,calc}$ **. Lay off the calculated values of $K_{d,calc}$ on the previously plotted graph. Next find the Harned coefficient (see Fig. 1.2) and evaluate $\gamma'_{\pm}$. Introducing the corresponding values into

* Prepare the solutions by mixing a 6 M solution of $UO_2(NO_3)_2$, 4 M $Ca(NO_3)_2$, and water in amounts determined by calculation.

** Use the experimental values of the constant K in the calculations.

formula (1.17), calculate $K_{d,calc,cor}$ in the presence of a salting out agent. Compare the calculated values with the experimental results. Make conclusions on the applicability of the above equations for calculating the distribution coefficients of uranium.

Experiment 1.2. EXTRACTION OF Fe^{III}

FROM HYDROCHLORIC ACID SOLUTIONS

WITH ETHERS [1, 4, 7]

At low concentrations of Fe^{III} , the coefficient of its distribution between the aqueous and organic phases depends only on the concentration of the hydrochloric acid. At high concentrations, polymerization of the compound being extracted occurs in the organic phase, and therefore the coefficient of distribution of Fe^{III} depends greatly on its concentration in the aqueous phase.

In the given experiment, it is exactly this relation that is studied, and also the dependence of the coefficient of distribution of Fe^{III} on the concentration of the hydrochloric acid. In addition, the possibility of coextraction of Sb^{III} when extracting Fe^{III} is studied.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of γ -radiation (the crystal of the counter has a well for accommodating radioactive sources inside the scintillator). A shaker. Test tubes for measuring the radioactivity of the solutions (20). Test tubes for 5-10 ml with ground-glass stoppers for extraction (20). Bottles for 10-50 ml with ground-glass stoppers (20). Pipettes with a syringe for 1 and 2 ml.

Radioactive Substances. A solution of $FeCl_3$ in 10 M hydrochloric acid containing ^{59}Fe having a volume specific activity of 5×10^3 cpm/ml and a mass specific activity of at least 2 GBq/g (50 mCi/g). A solution of $SbCl_3$ in 8 M hydrochloric acid containing ^{124}Sb or ^{125}Sb with a total concentration of Sb^{III} equal to 10^{-6} - 10^{-3} mol/litre and a specific activity of 10^5 to 5×10^5 cpm/ml.

Reagents. Dipropyl, diisopropyl, or dibutyl ether. Solutions: $FeCl_3$ in 10 and 8 M hydrochloric acid containing 10^{-3} , 10^{-2} , 10^{-1} , and 1.0 mol/litre of Fe^{III} .

Performance of Work

By mixing the solutions of $FeCl_3$ and $^{59}FeCl_3$ in 10 M hydrochloric acid, an HCl solution, and water, prepare in the bottles 5-10 ml each of solutions containing 10^{-3} mol/litre

of Fe^{III} in 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 M hydrochloric acid. In a similar way, prepare solutions of 7 M with respect to HCl and containing 10^{-3} , 10^{-2} , and 10^{-1} mol/litre of Fe^{III} .

Note. In preparing the solutions, one may disregard the mass content of ^{59}Fe in the solution. All the solutions must have an identical volume specific activity equal to $5 \times 10^3/10^4$ cpm/ml.

(a) General Procedure for Determining Distribution Coefficient of Fe^{III}

The distribution coefficients of Fe^{III} are determined as follows. Put 2 ml each of one of the prepared hydrogen chloride solutions of radioactive iron into two test tubes with ground-glass stoppers. Put into each of the same tubes 2 ml of dipropyl ether* preliminarily saturated with hydrochloric acid to the same concentration. Fasten the test tubes in the laboratory shaker and mix the phases during the required time [see (b)]. Extract the tubes, and after separation of the solution take 1 ml from each phase with a pipette and syringe and put the samples into test tubes for measuring the activity. Measure the activity using a γ -scintillation counter. The ratio of the activities in the organic and aqueous phases is used to determine K_d for $^{59}\text{Fe}^{\text{III}}$.

(b) Achievement of Thermodynamic Equilibrium

To determine the time needed for equilibrium to set in, find the Fe^{III} distribution coefficients in 5 M hydrochloric acid (the iron concentration is 10^{-3} mol/litre) after mixing the phases for 1, 5, 10, 20, 30, and 60 min.

Depict the results obtained graphically, and find the time needed for equilibrium to set in.

To verify whether true thermodynamic equilibrium does indeed set in during this time, determine consecutively the distribution coefficients upon extraction and reextraction, for example from a solution of 5 M HCl and 10^{-3} mol/litre of Fe^{III} .

* Diisopropyl, di- n -butyl or diisobutyl ether may be used. The ether used must not contain organic peroxides that reduce iron(III) to iron(II) which cannot be extracted (test for a peroxide using a 1 M KI solution with starch).

After mixing the phases during the previously found time, determine the distribution coefficient. Next separate the phases and put them into different test tubes. Further, add equal volumes of preliminarily saturated solutions (5 *M* hydrochloric acid saturated with ether to the organic phase, and dipropyl ether saturated with 5 *M* hydrochloric acid to the aqueous phase). Determine the distribution coefficients for extraction and reextraction. Equality of all three distribution coefficients obtained indicates that true thermodynamic equilibrium sets in in the system being studied.

*(c) Dependence of Fe^{III} Distribution
Coefficient on Concentration
of Hydrochloric Acid in Aqueous Phase*

Determine the Fe^{III} distribution coefficients between acid solutions (1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 *M*) and dipropyl ether preliminarily saturated with hydrochloric acid of the corresponding concentrations. All the solutions have the same (10^{-3} mol/litre) concentration of the Fe^{III} . Plot the results obtained on a graph (K_d versus c_{HCl}). Appraise the error in determining K_d . Find the concentration of hydrochloric acid at which the maximum extraction of the iron into the organic phase is observed.

*(d) Dependence of Distribution
Coefficient of Fe^{III} on Its Concentration
in the Aqueous Phase*

Determine the distribution coefficients of Fe^{III} between dipropyl ether and 6 or 7 *M* HCl at a varying iron concentration (10^{-3} , 10^{-2} , 10^{-1} , and 1 mol/litre). Plot the values of K_d versus the concentration of Fe^{III} in the aqueous phase.

(e) Coextraction of Sb^{III} with Fe^{III}

To study the phenomenon of coextraction, determine the distribution coefficients of Sb^{III} containing a radioactive isotope in the presence and in the absence of inactive Fe^{III} . Find the distribution coefficients of Sb^{III} in the same way as for Fe^{III} by stirring the phases during 5-10 min.

Put 2 ml each of solutions of 6 or 8 *M* HCl and containing 10^{-3} , 10^{-2} , 10^{-1} , and 1 mol/litre of Fe^{III} into test tubes

for extraction. Introduce into each tube 1 ml of a solution of a radioactive antimony compound in 6 or 8 *M* hydrochloric acid and 2 ml of dipropyl ether saturated with 6 or 8 *M* hydrochloric acid. Thoroughly mix the phases, let them settle, take 1 ml from each of the aqueous and organic phases and put the samples into test tubes for measuring the activity. Calculate the distribution coefficient of Sb^{III} in the presence and in the absence of Fe^{III} . Plot $K_{\text{d},\text{Sb}}$ versus $[\text{Fe}]_{(2)}$.

Explain why the distribution coefficient of Sb^{III} changes when the concentration of Fe^{III} is increased.

Experiment 1.3. SEPARATION OF $^{90}\text{Sr}^{2+}$ AND $^{90}\text{Y}^{3+}$ BY EXTRACTION WITH 8-HYDROXYQUINOLINE IN CHLOROFORM [6, 7]

The strontium radioactive isotope ^{90}Sr is obtained upon the fission of uranium. After its separation from the fission products, the daughter isotope ^{90}Y accumulates in it. The present experiment deals with how to find the optimal conditions for separating $^{90}\text{Y}^{3+}$ from $^{90}\text{Sr}^{2+}$ by extraction of their compounds with a chloroform solution of 8-hydroxyquinoline.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. Screens (10-15) of aluminium 0.1 mm thick. A shaker. An evaporation lamp. A pH meter. Test tubes for extraction for 15-20 ml with ground-glass stoppers. Pipettes with syringes for 1 and 10 ml. Measuring flasks for 100 ml. Glass bowls for measuring activity.

Radioactive Substances. A neutral solution of $\text{Sr}(\text{NO}_3)_2$ containing ^{90}Sr without a carrier in equilibrium with ^{90}Y having an activity of 1.5×10^6 cpm/ml.

Reagents. Chloroform. Solutions: 0.01, 0.1, and 1 *M* 8-hydroxyquinoline in CHCl_3 ; 0.1 *M* HCl ; 0.01 *M* $\text{Sr}(\text{NO}_3)_2$ and $\text{Y}(\text{NO}_3)_3$ [$\text{La}(\text{NO}_3)_3$ may be used]; and buffer solutions with $\text{pH} = 5, 6, 7, 8, 9, 10, 11,$ and 12 (an acetate or any other universal buffer solution may be used).

Performance of Work

The work is performed with radioactive isotopes ^{90}Sr and ^{90}Y without a carrier, therefore noticeable adsorption of the isotopes on glass is possible. To reduce the adsorption

of $^{90}\text{Sr}^{2+}$ and $^{90}\text{Y}^{3+}$ by the walls of the glassware, it must be saturated with the relevant salts. For this purpose, rinse all the glassware to be used with a 0.1 *M* solution of $\text{Sr}(\text{NO}_3)_2$ and $\text{Y}(\text{NO}_3)_3$ [$\text{La}(\text{NO}_3)_3$ may be used]. Next pour out the solutions and thoroughly wash all the walls with the corresponding (for the given experiment) buffer solution. Remove the buffer solution.

Introduce 5 ml of a 0.1 *M* solution of 8-hydroxyquinoline in chloroform, 4 ml of a buffer mixture with the required pH, and 1 ml of a solution of ^{90}Sr in the form of $\text{Sr}(\text{NO}_3)_2$ (with a specific radioactivity of 1.5×10^5 cpm/ml) into a test tube with a ground-glass joint.

Close the tube with a stopper and mix its contents in the shaker during the required time. Next extract the tube and after complete separation* take 1 ml each of the aqueous and organic phases, place the samples into the glass bowls for measuring the activity, carefully evaporate them under the lamp until dry, and measure the activity.

The determination of the radioactivity of ^{90}Sr and ^{90}Y upon their joint presence is based on the difference between the maximum paths of β -particles of these isotopes. The total radioactivity (counting rate) of a source without a screen is

$$I_{s+b} = I_{\text{Sr}} + I_{\text{Y}}$$

The radioactivity of the source with the screen I_{scr} is

$$I_{\text{scr}} = I_{\text{Y}}e^{-\mu d}$$

where μ is the mass absorption coefficient of β -particles, and d is the thickness of the layer in which complete absorption of the ^{90}Sr β -particles occurs.

Consequently, the radioactivity of ^{90}Y will be $I_{\text{Y}} = I_{\text{scr}}e^{\mu d}$, and $I_{\text{Sr}} = I_{s+b} - I_{\text{scr}}e^{\mu d}$. The distribution coefficient K_d is determined for each isotope.

(a) Extraction Kinetics

Extract the compounds of ^{90}Sr and ^{90}Y with a 0.1 *M* chloroform solution of 8-hydroxyquinoline from a buffer aqueous solution at pH = 9, shaking the contents of the test

* Separation of the phases can be accelerated by centrifuging.

tubes during 1, 5, 10, 15, 20, and 30 minutes. Find the effective distribution coefficient $K_{d,eff}$ by dividing the total activity of 1 ml of the organic phase by the total activity of 1 ml of the aqueous phase (the measurement without a screen). Plot $K_{d,eff}$ versus the duration of mixing the phases, and find the minimum time needed for extraction equilibrium to set in. Mix the phases during this time in all the following experiments.

*(b) Influence of pH of Aqueous Solution
on Separation Coefficient*

Extract the compounds of ^{90}Sr and ^{90}Y with a 0.1 M chloroform solution of 8-hydroxyquinoline from aqueous solutions with a pH of 5, 6, 7, 8, 9, 10, and 12. Check the pH of the aqueous equilibrium solution with the aid of a pH meter or a universal indicator. Determine the distribution coefficient of ^{90}Sr and ^{90}Y and their separation coefficient. Plot α versus pH and find the pH at which the maximum separation coefficient is obtained.

*(c) Influence of Concentration
of 8-Hydroxyquinoline in Organic Phase
on the Separation Coefficient of ^{90}Sr and ^{90}Y
and on the Extraction of ^{90}Y into
the Organic Phase*

Extraction is performed at the chosen pH of the aqueous solution with chloroform solutions of 8-hydroxyquinoline with a concentration of 0.01, 0.1, and 1.0 M. Plot K_d versus the extracting agent concentration and find the optimal concentration of the 8-hydroxyquinoline in chloroform. (When finding the optimal concentration of 8-hydroxyquinoline, take into account not only the separation coefficient of $^{90}\text{Sr}^{2+}$ and $^{90}\text{Y}^{3+}$, but also the per cent of extraction of $^{90}\text{Y}^{3+}$ in single extraction.)

*(d) Separation of ^{90}Sr and ^{90}Y
and Proof of Their Radioactive Purity*

Calculate the required number of consecutive extractions for removing 99.98% of the $^{90}\text{Y}^{3+}$ (the volumes of the aqueous and organic phases are equal).

Separate the $^{90}\text{Sr}^{2+}$ and $^{90}\text{Y}^{3+}$ in the extraction conditions found to be optimal. For this purpose, put an amount of the initial solution into a separatory funnel such that the activity of each isotope will be about 10^6 cpm. Provide the required pH in the aqueous phase and extract the $^{90}\text{Y}^{3+}$ several times with a chloroform solution of 8-hydroxyquinoline (using the optimal concentration of the latter). Wash the $^{90}\text{Sr}^{2+}$ from the organic phase with an aqueous solution having the selected pH (it is necessary to purify the ^{90}Y from the ^{90}Sr by 99.98%).

Check the radiochemical purity of the ^{90}Y and ^{90}Sr sources. To do this, determine the distribution coefficients upon the consecutive twofold extraction of both isotopes. The constancy of the relevant distribution coefficients points to the chemical purity of the ^{90}Y and ^{90}Sr .

Radioactive isotopes are customarily used in aqueous solutions. Therefore, the $^{90}\text{Y}^{3+}$ is reextracted with an aqueous solution having the required pH [see (b) of this experiment].

To check the radiochemical purity of the isotopes, perform physical identification of each of them.

Prepare sources of ^{90}Sr and ^{90}Y by evaporating aqueous solutions of the corresponding compounds under a hood in glass bowls. Determine the maximum energy of the β -particles of ^{90}Sr and ^{90}Y and compare it with the tabulated values. Determine the half-life of ^{90}Y .

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Chapter 2 Distribution of Radioactive Isotopes Between Liquid and Solid Phases

THEORETICAL INTRODUCTION [1-4]

When a solid phase separates from a solution in systems that contain an impurity (microcomponent) in addition to the main component (macrocomponent), the transition of the microcomponent into the bulk and (or) onto the surface of the formed solid phase is often observed. The migration of a microcomponent from a solution into a precipitate may also be due to processes of ripening of a previously formed solid phase. If in interphase migration a microcomponent forms no own solid phase, the process is called **coprecipitation**. Coprecipitation with the participation of a crystalline solid phase when a microcomponent is distributed over the bulk of the precipitate is called **cocrystallization**.

When a solid phase is used whose structure is close to perfection, the microcomponent mainly accumulates at the phase interface. In this case, the process is called **adsorption** of the microcomponent by the solid sorbent.

It is convenient to watch the behaviour of a microcomponent in processes of heterophase distribution with the aid of radioactive isotopes.

A. COCRYSTALLIZATION

The formation of a precipitate is attended by the formation, growth, and structural recrystallization of the particles of the solid phase and its ripening. A microcomponent in the solution participates in each of these processes, which makes the general picture of cocrystallization quite involved. Sometimes, however, the laws of transition of radioactive isotopes into a precipitate are quite simple. Two very simple kinds of **non-equilibrium distribution** of a microcomponent between the precipitate and solution in cocrystallization are distinguished—**logarithmic** and **linear**.

If a precipitate separates from a slightly supersaturated solution and consists of quite large slowly growing and therefore perfect crystals, while the surface of the precipitate at any instant of termination of the supersaturation is in equilibrium with the liquid phase, the cocrystallization of microamounts of radioactive isotopes is described by the logarithmic or Doerner-Hoskins distribution law:

$$\ln \frac{x_0}{x_0 - x} = \lambda_0 \ln \frac{y_0}{y_0 - y} \quad (2.1)$$

where x_0 and y_0 are the amounts of the micro- and macrocomponent in the system, x and y are the amounts of micro- and macrocomponents in the precipitate, and λ_0 is the coefficient of surface cocrystallization characterizing the equilibrium distribution of a microcomponent between the surface layer of the precipitate and the solution. A distribution described by formula (2.1) is known as a logarithmic one. In a logarithmic distribution, the microcomponent is distributed non-uniformly over the bulk of the precipitate.

If a precipitate separates from a solution with moderate supersaturation and consists of rapidly growing, but nevertheless perfect crystals not inclined to recrystallize, while the surface of the precipitate does not have time to reach equilibrium with the entire liquid phase, but at any instant of precipitation is in equilibrium with the solution directly adjoining the phase interface, cocrystallization is described by the formula

$$\frac{x}{y} = \frac{\lambda_0 x_0}{y_1 + (y_0 - y_1) \lambda_0} \quad (2.2)$$

where y_1 is the amount of the macrocomponent in its saturated solution. A distribution proceeding in accordance with formula (2.2) is called linear. In a linear distribution, the microcomponent accumulates uniformly in the precipitate as the mass of the latter grows.

In cocrystallization from a highly supersaturated solution, an imperfect precipitate forms, as a rule. It rapidly ripens and recrystallizes. In the process of recrystallization and ripening, intensive migration of the microcomponent in the solid phase and its interphase redistribution occur. As a result, in a short interval after the formation of a precipitate, **equilibrium distribution** of the radioactive isotope between the volumes of the solid and liquid phases

takes place. This distribution obeys V. Khlopin's law and is described by the Henderson and Kraček formula:

$$\frac{x_{eq}}{y_{eq}} = D \frac{x_0 - x_{eq}}{y_0 - y_{eq}} \quad (2.3)$$

where x_{eq} and y_{eq} are the equilibrium amounts of the micro- and macrocomponent in the precipitate, and D is the equilibrium coefficient of cocrystallization.

The coefficient D does not change upon an increase in the mass of the precipitate and the microconcentration of the radioactive isotopes in the solution. Its value depends on the temperature, the phase composition, and the state of the microcomponent in the solution and precipitate.

The influence of the composition of a solution manifests itself especially sharply if complexing agents binding the microcomponent into non-precipitating complexes are introduced into the system. If the amount of introduced complexing agent is commensurable with the amount of the macrocomponent in the solution, at a constant ionic strength of the solution the coefficient D varies with an increase in the concentration of the complex molecules of the macrocomponent according to the equation

$$\frac{1+\Phi}{D} = \frac{1}{D} + \frac{\beta_1\Phi}{\beta_2 D_0} \quad (2.4)$$

where Φ is the ratio of the amounts of the macrocomponent in the complex and non-complex forms, D_0 is the coefficient of cocrystallization at $\Phi = 0$, β_1 and β_2 are instability constants of the micro- and macrocomponent complexes.

Upon the coprecipitation of a microcomponent with sparingly soluble hydroxides that are in great favour in radiochemistry as collectors, the coefficient D is sensitive to the pH of the solution. The dependence of the coprecipitation on the pH is usually a complicated one. But if the hydrogen ions simply "compete" for places in the solid phase with the ions of the microcomponent that does not change its state in the solution when the pH changes, the following relation is observed:

$$\log D = \log \overset{0}{D} + n \text{ pH} \quad (2.5)$$

where $\overset{0}{D}$ and n are parameters associated with an elementary event of exchange of hydrogen and microcomponent ions in the solid phase.

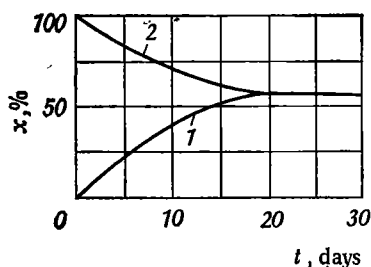


Fig. 2.1.

Kinetics of change in the amount of the microcomponent in the solid phase when Ra is precipitated with $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ crystals in conditions of the isothermal recrystallization of the macrocomponent in a saturated solution:

1—achievement of equilibrium from "below"; 2—achievement of equilibrium from "above"

The most reliable way of determining the coefficient D is isothermal recrystallization of a finely dispersed precipitate of the macrocomponent in its saturated solution when the system contains a distributing radioactive isotope. If at the initial instant of recrystallization the radioactive isotope is only in the solid phase, the proceeding of recrystallization is attended by an increase in the concentration of the microcomponent in the solution. This leads to acceleration of the transition of the radioactive isotope from the liquid phase to the solid one and to the establishment of dynamic equilibrium in the system (the achievement of equilibrium from "above") (Fig. 2.1, curve 2). The system arrives at the same state if the radioactive isotope at the initial instant of recrystallization is present only in the liquid phase, and recrystallization produces a reduction in the concentration of the microcomponent in the solution until a state of dynamic equilibrium is achieved (the achievement of equilibrium from "below") (Fig. 2.1, curve 1). Measurement of the concentration of a microcomponent in the phases of a system in a state not depending on how it is achieved makes it possible to determine the coefficient D .

A way of determining D is sometimes possible that uses the ability of precipitates to intensively recrystallize in the process of their separation from a supersaturated solution (the method of the isothermal elimination of supersaturation). When using this method, a highly supersaturated

solution of a macrocomponent containing a radioactive isotope is intensively agitated during three or four hours, as a result of which a precipitate that has recrystallized many times separates from the solution.

B. ADSORPTION

The prolonged ageing of the solid phase in a saturated solution of a macrocomponent leads to a state in which the microcomponent penetrates into the bulk of the precipitate negligibly slowly, and the interaction of the radioactive isotope with the stable solid phase formed in the ageing process is limited to adsorption. The adsorbed radioactive isotope may be retained by the surface layer of the solid phase (**primary adsorption**) or by the adsorbed layer of the solution directly adjoining it (**secondary adsorption**).

Primary adsorption is the first stage in the transition of a radioactive isotope from a solution into the solid phase and is described by an equation similar to (2.3):

$$\frac{x_{\text{eq}}}{x_0 - x_{\text{eq}}} = \lambda_0 \frac{y'}{y_0 - y} \quad (2.6)$$

where $y' = ysl\rho$ is the amount of the macrocomponent in the surface layer of the solid phase, s is the specific surface area of the precipitate, l is the thickness of the surface layer, and ρ is the density of the solid phase. The coefficient λ_0 depends on the temperature and composition of the system's phases. We may use formulas (2.4) and (2.5) to describe the influence of the composition of a solution on primary adsorption if we substitute the coefficient λ_0 for D in them.

Secondary adsorption is due to Coulomb (**electrostatic adsorption**) or van der Waals (**molecular or dispersion adsorption**) forces. In electrostatic adsorption, the radioactive isotope is retained by active centres charged oppositely to the charge of the radioactive isotope ions. Ions of the solution having an increased ability of being adsorbed on the surface of the solid phase (**potential-forming ions**) may be such centres. If the charge of the potential-forming ions is opposite to that of the microcomponent ions, while the ions of like charge with those of the microcomponent are

singly charged and do not change their concentration in the course of its adsorption, the following expression holds:

$$\left(\frac{x}{x_0 - x}\right)^{1/2} \approx A + B \ln c \quad (2.7)$$

The constants A and B can be determined by analysing the experimentally found dependence of the factor $[x/(x_0 - x)]^{1/2}$ on the logarithm of the concentration of the potential-forming ions. The constants A and B are related to the jump in the normal potential on the surface of the solid phase by the expression

$$\Phi_0 \approx \frac{BRT}{AzF} \quad (2.8)$$

where R is the molar gas constant, T is the absolute temperature, z is the absolute value of the charge of a potential-forming ion, and F is the Faraday constant.

Molecular adsorption occurs on the entire surface of the solid phase and with microconcentrations of the radioactive isotope is characterized by the linear isotherm

$$c_s = \alpha c_{sln} \quad (2.9)$$

where c_s is the equilibrium surface concentration of the microcomponent in the adsorbed layer, $\mu\text{Ci}/\text{cm}^2$, c_{sln} is the volume concentration of the microcomponent in the solution, $\mu\text{Ci}/\text{cm}^3$, and α is the adsorption coefficient. The latter in a number of cases exponentially falls off with increasing temperature:

$$\alpha = A \exp(E_a/RT) \quad (2.10)$$

where A is a constant with an unchanging composition of the phases, and E_a is the molar energy of adsorption.

To determine the coefficients λ_0 , A , B , or α , one must study coprecipitation in conditions in which virtually the entire coprecipitated radioactive isotope is retained by the phase interface. The failure of the coefficients λ_0 and α to depend on the specific surface area of the solid phase is a strict proof of the adsorption nature of coprecipitation. Upon prolonged preliminary stabilization of the solid phase guaranteeing slow incorporation of the radioactive isotope into the precipitate, however, a high rate of coprecipitation producing equilibrium of the system in 20-30 min may be

considered as a proof of the adsorption nature of coprecipitation.

The time needed for the required preliminary stabilization of the solid phase is determined by its nature. Virtually insoluble materials such as polytetrafluoroethylene (Teflon) or glass in water require no stabilization, whereas substances with an appreciable solubility (for example, BaSO_4 and PbSO_4 in water) require prolonged stabilization in their saturated solution. Stabilization of the solid phase can be combined with another important operation preceding the studying of the adsorption of radioactive isotopes—purification of the precipitate from previously sorbed contaminants. Decanting washing can be used for this purpose. A major part of the mother liquor that was in prolonged contact with the precipitate and desorbed part of the impurities is systematically decanted from the stabilized solid phase and replaced with pure washing liquid in which stabilization of the precipitate continues. If the stabilized and purified solid phase is to be used as an adsorbent, it must not be freed from the washing liquid because contact of the precipitate with the air leads to deterioration of its stability and to contamination. To retain the stability and purity of the adsorbent when studying adsorption, one must introduce the precipitate into a system as a suspension, the amount of the solid phase in 1 ml of which has been determined beforehand by one of the analytical methods. When the precautions listed above are observed, the studying of adsorption does not involve any special difficulties and leads to definite results.

When studying adsorption, one must choose conditions for the experiments such that the change in the concentration of a solution as a result of adsorption will be large enough, and its accurate measurement will be possible. One must never try to make this change too large because for this purpose it is necessary to increase the mass of the solid phase introduced into the solution too much. It is most convenient that when studying adsorption, the condition $x_{\text{sln}} \approx x_0 - x_{\text{sln}}$ be observed. In primary adsorption, for example, this condition, according to formula (2.6), is equivalent to the requirement that

$$y \approx \frac{LV}{\rho \lambda_0 s l} \quad (2.11)$$

where $LV = y_0 - y$, L is the solubility of the solid phase, and V is the volume of the solution.

The studying of the laws of adsorption and coprecipitation of radioactive isotopes with precipitates is of a major practical significance associated with the use of these phenomena for studying the state of a substance in ultralow concentrations, for obtaining radiochemically pure substances, and for concentration and separation of carrier-free radioactive isotopes. The knowledge of the laws of sorption of radioactive isotopes made it possible to develop a number of effective sorption methods of their separation (fractional crystallization, coprecipitation with an isotope carrier, etc.).

When developing ways of separating a mixture of radioactive isotopes by means of sorption, one must first determine the ability of each component of the mixture to be adsorbed and coprecipitated with the selected macrocomponent, and then provide conditions facilitating the maximum development of the process that leads to sorption of only the radioactive isotope being separated. If we succeed in choosing a macrocomponent that sorbs only the radioactive isotope being separated, the mechanism of transition of the microcomponents into the solid phase stops playing a role. Here upon separation, one tends to increase the ability of the solid phase both to coprecipitate and to adsorb, using as sorbents the newly formed precipitates having a developed active surface and an imperfect structure.

The separation of radioactive isotopes by coprecipitation and adsorption, as a rule, does not require intricate equipment and large expenditures of time, which has given it great favour in radiochemical practical work.

Experiment 2.1. LOGARITHMIC DISTRIBUTION OF A MICROCOMPONENT IN THE ISOTHERMAL EVAPORATION OF A MACROCOMPONENT SOLUTION IN THE PRESENCE OF A PRECIPITATE [5]

The isothermal evaporation of a saturated macrocomponent solution in the presence of a precipitate provides favourable conditions for the logarithmic distribution of the microcomponent present in the solution. When the solvent evaporates, the solution becomes supersaturated. If the solution contains crystals of the macrocomponent, they grow, eliminating the supersaturation. The simultaneous evaporation of

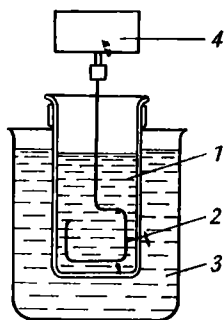


Fig. 2.2.

Device for studying logarithmic distribution of radioactive elements between solid and liquid phases:

1—beaker with solution; 2—agitator; 3—thermostat; 4—Warren motor

the solvent and growth of the crystals result in virtually constant supersaturation of the solution setting in. The magnitude of this supersaturation is the smaller, the larger is the mass of the precipitate, the more intensive is agitation of the solution, and the lower is the rate of evaporation of the solvent. An intelligent choice of these three conditions of coprecipitation makes it possible to study the distribution of the microcomponent at a low supersaturation at which the distribution does not depend on the intensity of solvent evaporation, and formula (2.1) may be applied. This is observed, for example, in the system $\text{NiSO}_4\text{-}^{60}\text{Co}^{2+}\text{-H}_2\text{O}$.

Equipment and Reagents

Equipment and Utensils. A thermostat ensuring a temperature of $25.0 \pm 0.5^\circ\text{C}$. A counter for registering γ -radiation with a scintillation attachment. An analytical balance. Devices (3) for studying the distribution of the microcomponent (Fig. 2.2) with Warren motors (with a speed of 60 rpm). A motor for 50-100 W. A laboratory autotransformer. A mercury thermometer with graduations of 0.1°C . A round-bottom flask for 500 ml with an agitator. Beakers for 100 ml (3) with a diameter of 40 mm. Beakers for 250 ml (3) with a diameter of 65 mm. A beaker for 50 ml. Cylinders for 10 and 50 ml. Pipettes (2) for 1 ml with a syringe. Test tubes (9) for measuring γ -activity. Flasks for 25 ml (6). Glass agitators (6). Beakers with a filtering bottom No. 1 (6). Bunsen bottles (6). A funnel with a filtering bottom No. 1.

Radioactive Substances. A solution, saturated at room temperature, of NiSO_4 containing $^{60}\text{Co}^{2+}$, with a specific activity of 10^5 cpm/ml.

Reagents. A powder of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ obtained upon cooling a hot saturated solution of NiSO_4 and stabilized in this solution during 5-6 hours, and then dried at room temperature (not higher than 31°C) to a constant mass. Crystalline NiSO_4 . An NiSO_4 solution saturated at room temperature.

Performance of Work

Pour about 200 ml of the solution of NiSO_4 saturated at room temperature and prepared beforehand into the 500-ml round-bottom flask and add about 50 g of the solid $\text{NiSO}_4 \times 7\text{H}_2\text{O}$ to the flask. Place the latter in a thermostat at $25.0 \pm 0.5^\circ\text{C}$ and vigorously agitate the contents of the flask during 30 min. Next rapidly filter the solution (supernate) from the undissolved precipitate with the aid of the funnel with a No. 1 filtering bottom preliminarily connected to a water-jet pump via a Bunsen bottle (all the utensils needed for performing this operation and the following ones must be dry and cooled to room temperature). Into each of three 100-ml and three 250-ml beakers pour 50 ml of the filtrate and 1 ml of the solution of NiSO_4 saturated at room temperature and containing $^{60}\text{Co}^{2+}$ with a specific activity of 10^5 cpm/ml. Add to each of these beakers 1 g of the stabilized $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ powder. Secure the beakers in the thermostat so that the level of the liquid in them is below that of the water in the thermostat. Stir the contents of the beakers with the aid of Warren motors (see Fig. 2.2). After 10 minutes of stirring needed for homogenization of the solutions, switch off the motors and take 1 ml of the liquid from each beaker with a pipette, after which renew the stirring.

Transfer the liquid samples into the test tubes for measuring the activity. After taking each sample, wash the pipette with 1 ml of water, adding this water to the contents of the relevant test tube.

If the salt crystallizes in a pipette, use water heated to $60-70^\circ\text{C}$ for washing it. Measure the activity of the test tubes.

Use the results of the measurements to calculate the activity of the solutions at the instant of sampling them. Adopt the calculated activity as the activity I_0 of the initial satu-

rated solution because during the 10 minutes of stirring the concentration of the $^{60}\text{Co}^{2+}$ in the liquid medium does not have time to change. Extract the beakers consecutively from the thermostat in 2, 3, and 4 hours, respectively. Filter off the precipitate through the preliminarily weighed beaker with a filtering bottom No. 1, wash it with a solution of NiSO_4 saturated at room temperature, and leave it to dry in the air up to a constant mass (at least for 6-10 h). Weigh the beakers with the precipitates. Dissolve each precipitate in the minimum amount of water, transfer the solutions obtained into the 25-ml measuring flasks, and bring the volume of the solutions up to the mark using a solution of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ saturated at room temperature. The saturated solution of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ is intended for providing a medium with a standard absorptivity with respect to the β - and γ -radiation of the ^{60}Co . Determine the activity of the solutions in conditions identical to those used in determining the activity of the initial solutions, thoroughly stirring the contents of the test tubes prior to measuring the activity.

Use the results of the measurements to evaluate the activity I_s of the solid phase at different instants of evaporation.

Calculate the fraction of the coprecipitated microcomponent x/x_0 . Use the quantity x/x_0 and the results of determining the mass (y) of the $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ that transferred to the solid phase upon the evaporation of the solvent during coprecipitation to calculate the coefficient λ_0 by formula (2.1).

Take into account in the calculations that the solid phase contains 1 g of previously introduced $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ which captures no microcomponent, and that 1 ml was taken from the liquid phase to determine the activity of the initial solution. The density of the saturated solution at 25 °C is 1.38 g/cm³, and the solubility of nickel sulphate at this temperature is 104.5 g of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 g of water.

Compare the coefficients λ_0 determined upon coprecipitation in beakers of various diameters, the rate of evaporation of the solvent from which is different.

Experiment 2.2. LINEAR DISTRIBUTION OF A MICROCOMPONENT IN THE ISOTHERMAL CRYSTALLIZATION OF A MACROCOMPONENT FROM A SUPERSATURATED SOLUTION [6]

Linear distribution is observed upon the cocrystallization of microamounts of $^{110}\text{Ag}^+$ with NaCl in the conditions of the isothermal elimination of supersaturation. Supersaturated NaCl solutions are not stable, but their stability grows after holding them at an elevated temperature. Agitation of the solutions, on the other hand, sharply lowers their stability. Hence, if a supersaturated solution of NaCl is overheated, and then cooled without agitation, one can obtain a sufficiently stable solution convenient for studying isothermal crystallization. Crystallization from such a solution can be initiated by intensively agitating it. Crystals of NaCl grow quite large and perfect from a solution being agitated having a supersaturation of 3-10% and capture the microcomponent $^{110}\text{Ag}^+$ with a coefficient of surface cocrystallization considerably larger than unity.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A water-jet pump. An analytical balance. A motor ensuring a constant speed of rotation of the agitator (200-500 rpm). An agate mortar. Vessels for determining the solubility (Fig. 2.3). Beakers with a filtering bottom. Test tubes with a takeoff. A glass filter No. 1. A pipette for 1 ml. Pipettes for 5 ml with syringes. Flasks for 25 ml. Measuring cylinders for 50 ml (2). Beakers for 100 ml. A weighing bottle. Planchets (6) for 5 ml for measuring activity.

Radioactive Substances. An NaCl solution saturated at 25.0 °C and containing $^{110}\text{Ag}^+$, specific activity 6×10^4 cpm/ml.

Reagents. Crystalline NaCl. CCl_4 . Solutions of NaCl saturated at 25 °C and at room temperature.

Performance of Work

Introduce 0.2 g of NaCl salt ground to a powder, 30 ml of an NaCl solution saturated at 25.0 °C, and 1 ml of a solution containing $^{110}\text{Ag}^+$ with an activity approximately equal to 6×10^4 cpm/ml and saturated with the macrocomponent into a vessel for determining solubility (see Fig. 2.3). Fill the seal of this vessel with water. Place the vessel in a thermostat with a temperature of 70 °C, seeing that the vessel is

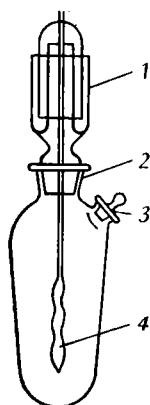


Fig. 2.3. Vessel for determining solubility:

1—water seal; 2—ground-glass joint; 3—offtake with ground-glass stopper for taking samples; 4—helicoidal agitator

immersed into the thermostating liquid almost up to offtake 3 (see Fig. 2.3). In the course of heating the vessel, periodically open the stopper of offtake 3 to prevent water getting into the vessel from the seal when the expanding air bubbles through the seal. Hold the vessel in the thermostat up to complete dissolving of the solid and then 10 minutes more. The time needed for dissolving of the solid, which sharply grows when the latter is ground poorly, must not exceed 10 minutes because otherwise the evaporation of the solvent becomes appreciable. Carefully transfer the vessel into a thermostat with a temperature of 25 °C, and cool it there in a quiet state during 20 minutes. In the course of cooling, periodically open the stopper of offtake 3, preventing water being sucked in from the seal to the vessel.

Prepare a device for filtration: connect a dried beaker with a filtering bottom through a test tube with an offtake pipe to a water jet pump.

If upon cooling, a precipitate appears from the solution in the thermostat, do not filter the liquid, but reheat it up to complete dissolving of the crystals and cool it again so as to obtain a supersaturated solution. When this is achieved (no crystals appear from the solution when it is cooled), stir the cooled supersaturated solution with the helicoidal agitator at a speed of 200-500 rpm until a precipitate ap-

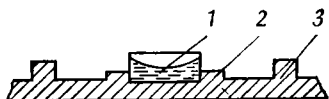


Fig. 2.4.

Planchet holder:

1—cupped planchet with radioactive solution; 2—limiting ring; 3—thermoplastic mount

pears, and then for one minute more. Rapidly filter the crystals that have appeared from the solution being agitated in the device prepared beforehand, after first switching on the pump. Add a definite amount (for example, 1 ml) of H_2O to the filtrate* and stir it, dissolving any precipitate that appears. Take off 3 ml of the supernate, transfer it with a pipette into a cupped planchet (for 5 ml) for measuring the activity of liquids that is placed in a special holder (Fig. 2.4) protecting the counter from contamination upon accidental spilling out of the solution, and measure the activity of the $^{110}Ag^+$. Transfer all the crystals remaining in the vessel into a beaker with a filtering bottom and wash them there with a saturated solution of NaCl until no activity remains in the washing liquid. Add 10 ml of CCl_4 to the precipitate accumulated at the bottom of the beaker. Stir the mixture with a glass rod to speed up the displacement of the mother liquor adsorbed by the precipitate and filter. Suck off the top layer together with the separated mother liquor with a pipette, and suck the remaining part through the filter. Weigh the beaker with the precipitate. Dissolve the precipitate on the filter in a minimum amount of water. Repeatedly wash the filter with a saturated solution of NaCl free of $^{110}Ag^+$. Pour the solution and the liquid used for washing the filter after dissolving the precipitate into a 25-ml measuring flask and bring its volume up to the mark with a saturated NaCl solution.

Measure the activity of the solution in conditions identical to those of measuring the activity of the first filtrate. Use the results of the activity measurements to calculate the relative amount of the microcomponent that has passed into the precipitate and remained in the solution by the instant of separation of the liquid and solid phases. Check

* The water is added to make up for its removal when the precipitate is sucked off.

the activity balance. According to the results of the radio-metric measurements and the determinations of the mass of the NaCl in the precipitate, calculate the relative concentration of the microcomponent in the solid phase $(1/y) \times (x/x_0)$ at the instant t of phase separation.

Simultaneously with the given experiment, run similar experiments with variation of the time t within the limits from 2 to 30 minutes.

Determine the independence of the quantity $x/(x_0y)$ of the recrystallization time. Use formula (2.2) to calculate the coefficient of surface cocrystallization λ_0 with a view to the solubility of NaCl at 25 °C being 0.317 g/ml.

To obtain a more complete picture of the coprecipitation of $^{110}\text{Ag}^+$ with NaCl, study how $x/(x_0y)$ depends on the mass of the macrocomponent in the solid phase by varying the mass of the NaCl precipitate (from 0.05 to 0.3 g) added to the initial saturated solution, and on the amount of $^{110}\text{Ag}^+$ in the initial liquid phase.

Experiment 2.3. EQUILIBRIUM DISTRIBUTION OF ISOMORPHIC MICROCOMPONENTS AND DETERMINATION OF COCRYSTALLIZATION COEFFICIENT [7]

The coprecipitation of $^{86}\text{Rb}^+$ and $^{131}\text{I}^-$ with KCl and KBr is an example of isomorphic cocrystallization. Potassium chloride and bromide are capable of rapid multifold recrystallization when precipitated from solutions with large and moderate supersaturations. It is therefore convenient to study equilibrium cocrystallization with these macrocomponents by the method of the isothermal elimination of supersaturation. The coefficient of cocrystallization of $^{86}\text{Rb}^+$ and $^{131}\text{I}^-$ with KCl and KBr is substantially smaller than unity. With low coefficients, which are widely encountered in radiochemical practice, account must be taken of the occlusion of the mother liquor, which may lead to capturing of considerable amounts of the microcomponent by the solid phase.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A thermostat for 25.0 ± 0.5 °C. An analytical balance. A drying cupboard (200-250 °C). An evaporation lamp. A vessel for determining solubility (see Fig. 2.3) with a helicoidal agitator onto whose

axle a bearing is mounted with the aid of a rubber packing. A motor connected to the agitator by a rubber tube. An autotransformer for controlling the voltage across the motor. A water jet pump. A Bunsen bottle for 1 litre provided with a rubber stopper and a glass tube. A water bath. A sampler consisting of a test tube with an offtake, a glass filter No. 1 (or 2), a rubber stopper with a glass tube onto which a vinyl chloride tube is fitted. Graduated pipettes for 1 ml (7-10) and 2 ml (1). A desiccator with CaCl_2 . A funnel. A glass spatula. A beaker for 20 ml (2). A syringe for 10 ml. Microweighing bottles (6). A porcelain beaker.

Radioactive Substances. A solution of K^{131}I or $^{86}\text{RbCl}$ with a specific activity of about 1×10^5 cpm/ml.

Reagents. Recrystallized KCl and KBr. Solutions of KCl and KBr saturated at room temperature. Calcined CaCl_2 (for the desiccator).

Performance of Work

Place the vessel for determining solubility with the helioidal agitator into the thermostat. Pour water into the seal. Connect the agitator to the motor and adjust the device so that when rotating at a speed of 500-1000 rpm the agitator does not touch the walls of the vessel.

Pour a weighed portion of the macrocomponent (KCl—4.45 g, KBr—8.10 g) into a 20-ml test tube. Add 1 ml of a solution of K^{131}I with an activity of about 1×10^5 cpm and 10 ml of water to the same tube. Heat the mixture on a water bath until the solid dissolves. Pour the solution obtained through a funnel heated in the drying cupboard (up to 40°C) into the vessel for determining solubility. Let the solution cool during 5 min and switch on the agitator.

After 1.5-2 h of continuous stirring, switch off the agitator, allow the solid phase to settle to the bottom of the vessel, and with the aid of preheated pipettes put 1 ml of the solution into each of three preliminarily weighed weighing bottles. Take a sample of the solid phase with the aid of the sampler. To do this, lower the end of the vinyl chloride tube onto the bottom of the vessel for determining solubility and connect the sampler to the water jet pump, closing the offtake (Fig. 2.5). When the main part of the precipitated solid phase is on the filter, open the offtake and distribute the precipitate into the three weighed weighing bottles with the aid of the glass spatula. (When working with a water jet pump, see that no radioactive solution gets from the test tube into the pump. To prevent contamination of the latter, install a Bunsen bottle as a trap.)

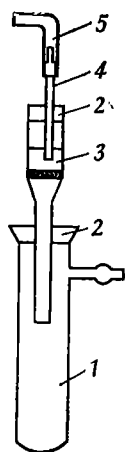


Fig. 2.5.

Sampler for phase separation:

1—test tube with offtake; 2—rubber stoppers; 3—glass filter No. 1 or No. 2; 4—glass tube; 5—vinyl chloride tube 4 mm in diameter

Weigh the weighing bottles with the solution and precipitate and dry them under the lamp. Next calcine them in the drying cupboard for 2-3 h at 200-250 °C. Weigh the weighing bottles cooled in the desiccator again and measure the activity of the dry residues of the solid phase I_s and the dry residues of the solution I_{sln} . To do this, pour 3 ml of water into a flat-bottom cupped planchet and measure the planchet's background I_b . Pour the water from the planchet into a beaker. Dry the planchet. Transfer 1.5 ml of water from the beaker into one of the weighing bottles with dry residues using a pipette and completely dissolve the precipitate. After measuring the volume of the solution formed with a pipette, transfer it into the planchet for measuring the activity. Wash the weighing bottle consecutively with two portions of a saturated solution of the macro component, each containing 0.5 ml, and add these portions to the solution in the planchet. The total volume of the liquid in the planchet should be 3 ml.

Stir the solution in the planchet with the glass spatula and measure the activity of the solution. Proceed similarly with the dry residues in the other weighing bottles. Since in the systems being studied, $D \ll 1$, the activity of the

dry residue of the solid phase may be only two or three times higher than the background of a planchet. Enter the results of determining the content of the macrocomponent in the samples of the solution and precipitate into Tables 1 and 2, and the results of measuring the activity into Tables 3 and 4.

From the results of determining the solubility L for three samples of the solution (see Table 1), find the mean value of the solubility $\bar{L}$, and from the results of measuring the activity of samples of the solution (see Table 3)—the mean value of $\bar{I}_{\text{sln}}/m_{\text{sln}}$.

Table 1. Results of Determining the Content of the Macrocomponent in Samples of the Solution

Weighing bottle				Solubility of salt in 1 g of water
No.	Mass m_1	Mass with sample m_2	Mass after calcination m_3	$L = \frac{m_2 - m_1}{m_3 - m_1}$

Table 2. Results of Determining the Content of the Macrocomponent in Samples of the Precipitate

Weighing bottle				Mass of sample $m_2 - m_1$	Mass of dry residue $m = m_3 - m_1$	Mass of water in sample $m_{\text{H}_2\text{O}} = m_2 - m_3$
No.	Mass m_1	Mass with sample m_2	Mass after calcination m_3			

Table 3. Results of Measuring Activity of Solution Samples

No. of weighing bottle	Mean background during 100 s I_b	Activity of solution samples		Activity of 1 g of solution $I_{\text{sln}}/m_{\text{sln}}$
		during 100 s I	without background $I_{\text{sln}} = I - I_b$	

Table 4. Results of Measuring Activity of Precipitate Samples

No. of weighing bottle	Background		Activity of precipitate sample		
	during time τ	during 100 s I_b	during time τ	during 100 s I	without background $I_{\text{s,b}} = I - I_b$

For each solid phase sample, calculate the content of the salt in the dry residue ($m_{\text{H}_2\text{O}}\bar{L}$) and the mass of the solid phase proper:

$$m_s = m - m_{\text{H}_2\text{O}}\bar{L}$$

We find the value of the coefficients D corresponding to three different samples of the precipitate. The coefficient D is evaluated as the ratio of the activity of 1 g of precipitate salt to the mean activity of 1 g of salt in the solution:

$$D = \frac{I_s}{m_s} \bigg/ \frac{\bar{I}_{\text{sln}}}{m_{\text{sln}}} = \frac{I_{s, b} - (\bar{I}_{\text{sln}}/m_{\text{sln}}) m_{\text{H}_2\text{O}}\bar{L}}{(m - m_{\text{H}_2\text{O}}\bar{L}) (\bar{I}_{\text{sln}}/m_{\text{sln}})}$$

Determine the mean value of D .

Experiment 2.4. INFLUENCE OF COMPLEXING AND TEMPERATURE ON THE ISOMORPHIC COPRECIPITATION OF $^{89}\text{Sr}^{2+}$ WITH CRYSTALS OF $\text{Ba}(\text{NO}_3)_2$ FROM AQUEOUS SOLUTIONS [8]

It is convenient to study the influence of complexing on the coprecipitation of radioactive isotopes using the example of the isomorphic coprecipitation of $\text{Sr}(\text{NO}_3)_2$ with $\text{Ba}(\text{NO}_3)_2$ in the presence of EDTA (ethylene diamine tetraacetic acid—complexon III). The complex ions of barium ethylene diamine tetraacetate are very stable, and the solubility of this complex compound is higher than that of $\text{Ba}(\text{NO}_3)_2$. Consequently, knowing the mass of the EDTA added to the solution, one may calculate the ratio of the amounts of barium in the complex and non-complex forms, equal to the ratio of the molar concentration of the EDTA to the solubility of barium nitrate. At the same time, the concentration of the free complexing agent due to the dissociation of the complex ions of barium is sufficiently high to bind the major part of the $^{89}\text{Sr}^{2+}$ into non-precipitating complexes that are more stable than barium complexes.

As a result, the distribution of the $^{89}\text{Sr}^{2+}$ between the precipitate of $\text{Ba}(\text{NO}_3)_2$ and its saturated solution in the presence of EDTA is described (at a constant ionic strength of the solution) by formula (2.4). To check this, one must separate the precipitate from a solution with a supersaturation above 30 g/litre, at which the precipitate intensively

ripens, so that already in 4-6 h after its separation, equilibrium distribution sets in in the system. To maintain a constant ionic strength, NaNO_3 should be added to the system.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A centrifuge. An analytical balance. Vessels for determining solubility (see Fig. 2.3) complete with motors and autotransformers (6 sets). A water bath. A thermostat for 20°C . Measuring cylinders for 20 and 25 ml. Centrifuge tubes for 10-15 ml (6). Beakers for 50 ml (6). Standard flat-bottom cupped planchets for measuring the activity of liquids, for 5 ml.

Radioactive Substances. A solution of $\text{Ba}(\text{NO}_3)_2$ saturated at 20°C , containing 500 g/litre of NaNO_3 and $^{89}\text{Sr}^{2+}$, with a specific activity of approximately 5×10^5 cpm/ml.

Reagents. Crystalline $\text{Ba}(\text{NO}_3)_2$, CCl_4 . Solutions: 0.16 *M* EDTA (sodium ethylene diamine tetraacetate); saturated of $\text{Ba}(\text{NO}_3)_2$ at 20°C and containing 500 g/litre of NaNO_3 ; saturated of $\text{Ba}(\text{NO}_3)_2$ at 20°C and at room temperature.

Performance of Work

Measure the activity of the initial solution containing $^{89}\text{Sr}^{2+}$, 500 g/litre of NaNO_3 and saturated with $\text{Ba}(\text{NO}_3)_2$. For this purpose, introduce 0.1 ml of the initial solution into a 25-ml measuring flask, bring the volume of the liquid in the flask up to the required level with a solution of $\text{Ba}(\text{NO}_3)_2$ saturated at room temperature, and agitate the ingredients. Transfer part of the solution (3 ml) into a flat-bottom standard cupped planchet for measuring the activity. On the basis of the results of measuring the activity, calculate the volume of the initial solution that would ensure an activity of $\sim 4 \times 10^3$ cpm.

Into each of the six vessels for determining solubility (see Fig. 2.3), introduce the calculated volume of the initial solution containing $^{89}\text{Sr}^{2+}$, 1 g of the salt $\text{Ba}(\text{NO}_3)_2$ and a varying amount (from 25 to 0 ml) of a solution of $\text{Ba}(\text{NO}_3)_2$ saturated at 20°C and containing 500 g/litre of NaNO_3 , and, accordingly, from 0 to 25 ml of a 0.16 *M* solution of EDTA saturated with $\text{Ba}(\text{NO}_3)_2$ and also containing 500 g/litre of NaNO_3 . The total volume of the added liquid phase in each vessel must be 25 ml.

Heat the vessels on a water bath up to complete dissolving of the solid phase, carefully transfer them into a thermostat at 20°C where they are held 10 min without stirring,

and then stir them for four hours with a helicoidal mechanical agitator, which results in complete elimination of the supersaturation in the supercooled initial solution. Stir the solution at an agitator speed of over 200 rpm to accelerate the elimination of supersaturation. Switch off the agitator. Transfer the content of each vessel into a separate beaker with a capacity of 50 ml. Take 3 ml from each beaker and measure the samples' activity in standard flat-bottom cupped planchets after first diluting the solution when needed with a saturated solution of $\text{Ba}(\text{NO}_3)_2$.

Use the results of the measurement to calculate the activity I_{sln} of the mother liquor at the instant of the complete elimination of the supersaturation. Next separate the precipitates from the mother liquor and determine their activity. For this purpose, carefully suck about 75-90% of the supernate from the beakers with a pipette, seeing that the latter takes up no precipitate. Transfer the remaining solution together with the precipitate into the test tubes for centrifuging and add 5 ml of CCl_4 to each of them. Thoroughly stir the mixtures with a rod and centrifuge them, which leads to displacement of the residues of the mother liquor from the surface of the precipitate and its accumulation over the layer of CCl_4 . Suck out the supernate from the centrifuge tubes with a pipette. To remove from the tubes the $^{89}\text{Sr}^{2+}$ contained in the mother liquor that you did not succeed in sucking out, carefully add 2 ml of a saturated solution of $\text{Ba}(\text{NO}_3)_2$ free of ^{89}Sr to each tube and then remove the added liquid with a pipette. Repeat the displacement of the mother liquor, for which purpose introduce 2 ml of a saturated solution of $\text{Ba}(\text{NO}_3)_2$ to each tube, stir the mixture, let the water layer settle over the layer of CCl_4 , and remove the water layer with a pipette.

Pour off the CCl_4 from the precipitates, dry the latter, and dissolve them in 10 ml of water. Determine the activity of the solution in conditions identical to those in which the activity of the mother liquor was measured. Use the results of measurement for calculating the activity I_s of the precipitate at the instant of elimination of the supersaturation. With a view to the solubility of $\text{Ba}(\text{NO}_3)_2$ in a solution with a concentration of 500 g/litre being $L = 7.8 \times 10^{-2} M$, calculate the values of the coefficient of equilibrium cocrystallization D_0 in the absence of the complexing agent, the relative amount Φ of the complex form of barium in the so-

lution, and the values of the coefficients of cocrystallization D for different contents of the complexing agent:

$$D_0 = \frac{I_s LV}{I_{s \ln y}} \quad \Phi = \frac{c V_c}{V L} \quad D = \frac{I_s LV (1 + \Phi)}{I_{s \ln y}}$$

where V is the volume of the solution from which a precipitate separates, y is the mass of the precipitate upon the complete elimination of supersaturation, and c and V_c are the concentration and volume of the EDTA solution added to the system.

Study graphically the experimentally found dependence of the factor $(1 + \Phi)/D$ on the value of Φ and compare this relation with that obtained by formula (2.4).

A similar procedure can be followed to establish the influence of the complexing agent concentration on the value of D at 0, 40, and 60 °C.

Experiment 2.5. INFLUENCE OF POLYVALENT IONS AND OF MICROCOMPONENT CONCENTRATION ON DISTRIBUTION OF AN ISODIMORPHIC SUBSTANCE BETWEEN A SOLUTION AND A PRECIPITATE OF A MACROCOMPONENT [9]

Barium chloride separating from aqueous solutions in the form of the crystals $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ of the monoclinic system is capable of coprecipitating the salt PbCl_2 crystallizing at 20 °C in the rhombic system. Mixed crystals are formed that are characterized by a coefficient D not depending on the concentration of the microcomponent in the system and on the presence of polyvalent ions in the solution. It is not difficult to convince oneself in the truth of this statement by studying how the coefficient D measured by the method of isothermal elimination of supersaturation depends on the concentrations of AlCl_3 and PbCl_2 in the liquid phase.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. An emanator with a platinum or gold plate containing 40 MBq (~ 1 mCi) of radiothorium or mesothorium. A thermostat. An analytical balance. A sealed box. A water bath. An evaporation lamp. Test tubes with ground-glass stoppers and oil seals (6). A mortar. A porcelain bowl. Pipettes for 1 and 2 ml with a syringe. A beaker. Standard bowls for measuring the activity.

Reagents. Recrystallized salt $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. Solutions: BaCl_2 saturated at 20°C ; 0.001 and 0.0001 M AlCl_3 acidified with HCl ; PbCl_2 with a concentration of 1×10^{-3} , 1×10^{-4} , and 1×10^{-5} g/ml.

Performance of Work

Wash off a radioactive deposit of thoron (the products of thoron decay) obtained on a platinum or gold plate exposed during 24 hours in an emanator with small portions of water containing 1×10^{-5} g/ml of PbCl_2 , and bring the total volume of the washing liquid up to 7-10 ml. Transfer 1 ml of the obtained active solution of lead chloride with a pipette into each of five 10-ml test tubes with ground-glass stoppers. Add to each tube 4 ml of a saturated BaCl_2 solution at 20°C and 1.5-2 g of a finely ground recrystallized salt $\text{BaCl}_2 \cdot \text{H}_2\text{O}$. Add to each of three of the tubes 1 ml of the initial solutions of PbCl_2 containing different amounts of the microcomponent (within the limits from 1×10^{-5} to 1×10^{-3} g/ml), and to each of the fourth and fifth tubes 1 ml of 1×10^{-3} and 1×10^{-4} M solutions of AlCl_3 . Close all the test tubes with their ground-glass stoppers and heat them on the water bath up to complete dissolving of the precipitate. Place the tubes into a thermostat maintaining a temperature of 20°C , where after holding in a quiet state during 15-20 min stir the contents of the tubes during four hours with helicoidal agitators introduced into the tubes through the oil seals.

Switch off the agitators, allow the precipitates to settle to the bottom of the test tubes, and pour off the mother liquors from the solid phase. Wash the precipitates with a saturated solution of BaCl_2 containing no PbCl_2 . Next analyse the solid phases and the mother liquor for their content of ^{210}Pb . For this purpose, transfer the precipitate into a weighing bottle, dissolve it in a minimum amount of water, and drop 0.2 ml of the solution obtained onto a filter placed in a bowl for measuring activity. Evaporate the solution under a lamp and measure the activity of the residue. Measure the activity of 0.2 ml of the mother liquor in a similar way.

Calculate the coefficients of cocrystallization by formula (2.3) according to the results of measuring the activity of the solution and precipitate, and also to data on the solubility of BaCl_2 in water (44.6 g of BaCl_2 in 100 ml of

water) and the calculated mass of the precipitate separated upon the elimination of supersaturation. Perform the calculations for various concentrations of PbCl_2 and AlCl_3 in the initial solution. To obtain a more accurate value of the quantity D , find the mass of the BaCl_2 in the solution after the elimination of supersaturation by evaporating the solution until dry and determining the mass of the residue. Convince yourself that D does not depend on the concentration of PbCl_2 and AlCl_3 .

Experiment 2.6. FORMATION OF ANOMALOUSLY MIXED CRYSTALS IN THE SYSTEM K_2SO_4 - $^{141}\text{Ce}_2(\text{SO}_4)_3$ -1.5 M HNO_3 [10]

Anomalous mixed crystals with microconcentrations of a radioactive isotope in the system and a constant temperature have a coefficient of cocrystallization D not depending on the amount of macro- and microcomponent in the solid and liquid phases, and in this respect do not differ from isomorphic mixtures. The mixed crystals K_2SO_4 - $^{141}\text{Ce}_2(\text{SO}_4)_3$ separating from a solution in 1.5 M nitric acid are an example of such a system. The coefficient of cocrystallization D upon the distribution of the cerium between the solution and the precipitate of K_2SO_4 can be determined by studying the coprecipitation of $^{141}\text{Ce}^{3+}$ upon the isothermal elimination of the supersaturation of the carrier solution.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A drying cupboard. A water jet pump. A thermostat with four vessels for determining solubility. An analytical balance. A water bath. A motor ensuring rotation of the agitators at a speed of 500-1000 rpm. A mortar. Glass filters No. 1 or No. 2. Pipettes for 0.02, 1, 3, and 20 ml. Weighing bottles (4). Beakers for 100 ml (4). Flat-bottom standard cupped planchets for measuring activity.

Radioactive Substances. A saturated solution of K_2SO_4 in 1.5 M HNO_3 containing $^{141}\text{Ce}^{3+}$ with a specific activity of 2×10^5 cpm/ml.

Reagents. Solutions: K_2SO_4 saturated at 20 °C in 1.5 M nitric acid and K_2SO_4 saturated at 20 °C in water; 1.5 M HNO_3 .

Performance of Work

Introduce 0.2-1.0 g of ground K_2SO_4 salt, 35-40 ml of a solution of K_2SO_4 in 1.5 M nitric acid saturated at 20 °C and 1 ml of a solution containing $^{141}\text{Ce}^{3+}$, with an activity

of 2×10^5 cpm/ml, into each of four vessels. Heat the mixtures on a water bath up to dissolving of the solid, hold them at 60°C for 30 min after dissolving of the solid for stabilization of the solution, cool in a thermostat up to 20°C without agitation during 20 min, and then stir with a helicoidal agitator at a speed of 500-1000 rpm during four hours, which ensures the complete elimination of supersaturation.

Separate the precipitates from the supernate by filtration through a glass filter No. 1 or No. 2. Take 3 ml from each filtrate and measure the activity of these samples in standard flat-bottom planchets. If needed, preliminarily dilute the solution with a saturated solution of K_2SO_4 in 1.5 M HNO_3 . Use the results of the measurements to calculate the activities of the mother liquors of K_2SO_4 at the instant of complete elimination of supersaturation. Wash the precipitates on the filter with 10 ml of a saturated solution of K_2SO_4 in 1.5 M HNO_3 , and then with the same volume of a saturated solution of K_2SO_4 in water. Transfer the washed precipitates into weighing bottles, dry them in the drying cupboard up to a constant mass, and dissolve in a minimum volume of 1.5 M HNO_3 , taking into account that the solubility L of K_2SO_4 in 1.5 M HNO_3 is 0.215 g per gramme of solution. Bring the volume of each of the solutions when necessary up to 5 ml with a saturated solution of K_2SO_4 in 1.5 M HNO_3 . Measure the activity of 3 ml of each of the solutions obtained in conditions identical to those for determining the activity of the mother liquors. Use the results of the measurements to calculate the activities I_s of the precipitates at the instant of complete elimination of supersaturation. Calculate the coefficient of cocrystallization for different masses of the precipitate using the following formula equivalent to formula (2.3):

$$D = \frac{I_s L m}{I_{s \ln y}}$$

where m is the mass of the saturated solution of K_2SO_4 in 1.5 M HNO_3 introduced into the system, and y is the mass of the precipitate.

For a more detailed acquaintance with the system, repeat the experiments, maintaining a constant mass of the ground salt (0.5 g) and varying the volume (0.01-2 ml) of the initial solution containing $^{141}\text{Ce}^{3+}$, which makes it possible to

determine how D depends on the concentration of the $^{141}\text{Ce}^{3+}$ in the solution at the instant of the complete elimination of the supersaturation.

Experiment 2.7. FORMATION OF ANOMALOUSLY MIXED CRYSTALS IN THE SYSTEM $\text{NaCl-PbCl}_2\text{-H}_2\text{O}$ AND THE SEPARATION OF RaD AND RaE [11]

Microamounts of lead when coprecipitated with NaCl are capable of becoming concentrated to a considerable extent in the solid phase with the formation of anomalously mixed crystals. The formation of anomalously mixed crystals in the system $\text{NaCl-PbCl}_2\text{-H}_2\text{O}$ can be used to separate the radioactive isotope of lead from a number of accompanying elements, particularly from the radioactive isotopes of bismuth.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. An analytical balance. A lamp for evaporation. A drying cabinet. A water bath. A motor with a mechanical agitator and an autotransformer. A thermometer. A device for obtaining a stream of hydrogen chloride. A porcelain mortar. A beaker with a filtering bottom. A Bunsen bottle. A water jet pump. Pipettes for 1.5 and 20 ml with a syringe. Flasks for 50 ml. A flat-bottom planchet with a diameter of 2-3 cm for measuring the activity of the precipitate. Beakers for 100 ml (2).

Radioactive Substances. A solution of RaD, RaE, and RaF obtained by dissolving the active deposit from old ampoules with radon having a specific activity of 5×10^4 cpm/ml.

Reagents. Crystalline NaCl. Ethyl alcohol. A solution of NaCl saturated at room temperature.

Performance of Work

Pour 20 ml of water and 1 ml of a solution of RaD, RaE, and RaF with an activity of 5×10^4 cpm/ml obtained by dissolving the active deposit on old ampoules with radon into a 50-ml flask. Separate the polonium isotope RaF by electrochemical means (see Experiment 4.3). Add NaCl to the solution of RaD and RaE in an amount needed to obtain a solution saturated at room temperature, having in view that the solubility of NaCl per gramme of H_2O is 0.3568 g at

10 °C, 0.3585 at 20 °C, and 0.3608 g at 30 °C. Heat the mixture on a water bath up to complete dissolving of the solid phase, and then cool it to room temperature.

Transfer part of the dissolved NaCl to the solid phase in one of the following ways:

(1) by evaporating 20-25% of the solvent on a water bath with the following mixing of the formed supersaturated solution with a mechanical agitator during one hour;

(2) by salting out from 10 to 50% of the total amount of the dissolved macrocomponent by passing hydrogen chloride through the initial solution during 5-10 minutes;

(3) by mixing the initial solution with 10-15 ml of ethyl alcohol with agitation.

Filter the precipitated solid phase from the supernate with the aid of the beaker with a filtering bottom (filter No. 3). Wash the precipitate on the filter twice with 5 ml of a saturated NaCl solution free of RaD and RaE, and then with 2 ml of ethanol, dry to a constant mass in a drying cabinet at 70-100 °C, and weigh it. Transfer a definite, accurately weighed part of the precipitate (~0.3 g) into a flat-bottom planchet with a diameter of 2-3 cm, uniformly distribute the precipitate over the bottom of the planchet, and measure the activity of the RaE in the substance immediately and in 5-7 days after its preparation, using an aluminium screen for absorbing the radiation of the RaD.

Measure the activity of the filtrate in a similar way. For this purpose, pour 5 ml of the filtrate into a 50-cm³ weighing bottle, evaporate it until dry under an infrared lamp, stir the dry residue and triturate it slightly in the porcelain mortar. Then transfer a part of it equal to the mass of the NaCl in the preparation for measuring the activity of the precipitate into a flat-bottom planchet. Measure the activity of the sample of the dry residue. According to the data on the activity of the RaE in both preparations immediately and in 5-7 days after their preparation, and using the law of radioactive decay of the mixture of the parent and daughter isotope, calculate the relative amount of RaE and RaD in the solid and liquid phases at the instant of completion of coprecipitation.

Use the data on the relative amount of RaD and RaE in the solid and liquid phases, and also the results of determining the mass of the NaCl in the initial solution and the precipitate to calculate the coefficient of cocrystallization of

microamounts of Pb and Bi with the precipitate of NaCl and calculate the degree of separation of the isotopes ^{210}Pb and ^{210}Bi .

Experiment 2.8. COPRECIPITATION OF $^{89}\text{Sr}^{2+}$ WITH PRECIPITATE OF HYDRATED OXIDE [12]

The coprecipitation of radioactive elements with precipitates of sparingly soluble substances separated from very highly supersaturated solutions, as a rule, occurs in conditions of the formation of a solid phase with an imperfect crystalline or amorphous structure. In such precipitates, the microcomponent rapidly diffuses into the solid phase, bringing it into equilibrium with the solution. An example of such coprecipitation is the capture of $^{89}\text{Sr}^{2+}$ upon the precipitation of $\text{MnO}_2 \cdot \text{H}_2\text{O}$ from aqueous solutions of permanganate. Here formula (2.3) may be used, in which the coefficient D depends on the structure of the precipitate that changes very slowly, and on the pH of the solution.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A centrifuge. A pH meter. A shaker. Test tubes with ground-glass stoppers for 10 ml (9). Pipettes for 1 ml with syringes (2). Burettes for 10 ml (2). Beakers for 100 ml (8). Measuring flasks for 25 ml (8). Centrifuge test tubes for 10 ml. Bowls for measuring activity (2).

Radioactive Substances. A solution containing $^{89}\text{Sr}^{2+}$ without a carrier, with a specific activity of approximately 1×10^6 cpm/ml.

Reagents. Solutions: 1% H_2O_2 ; 1% KMnO_4 ; NaCl with a concentration of 4 g/litre; 0.1 M BaCl_2 ; 0.05 N HCl .

Performance of Work

Determine the activity of the initial solution of $^{89}\text{Sr}^{2+}$. For this purpose, transfer 0.5 ml of this solution into a 25-ml measuring flask and bring the volume of the solution up to the graduation with water containing 4 g/litre of NaCl. Next pour 1 ml of the dilute solution into a standard bowl with a volume of 2 ml and measure the activity of the solution.

On the basis of the measurements, calculate the volume of the initial solution of $^{89}\text{Sr}^{2+}$ that would ensure an activity

of 1 ml of the dilute solution in the bowl for measuring activity equal to about 2000 cpm. Transfer the calculated volume of the initial solution into a 100-ml beaker and add to it an accurately measured volume of a 1% solution of KMnO_4 sufficient for precipitating 15 mg of MnO_2 .

Add a 1% solution of H_2O_2 to the mixture dropwise from a burette until the violet colour disappears. Determine the volume of the added hydrogen peroxide. Coagulate the brown sol formed with 40 ml of an NaCl solution with a concentration of 4 g/litre, determine the pH of the solution with the aid of a pH meter, and, adding from a burette a 0.05 *N* solution of HCl , bring the pH of the liquid phase up to the required value ($6 \leq \text{pH} \leq 12$).

Calculate the dilution of the initial solution containing $^{89}\text{Sr}^{2+}$, and according to the activity of the initial solution and its dilution calculate the activity I_0 the dilute solution would have in the absence of coprecipitation.

Pour the mixture over into a test tube with a ground-glass stopper and shake it for one hour. Next separate the precipitate by centrifuging and determine the activity of the centrifugate ($^{89}\text{Sr}^{2+}$) in conditions identical to those in which the activity of the initial solution containing $^{89}\text{Sr}^{2+}$ was determined.

The difference between the activity I_0 of the dilute solution and that of the centrifugate is used to calculate the relative amount of the microcomponent that has passed into the solid phase and determine the quantity $x/(x_0 - x)$ proportional to the coefficient D .

The quantity $x/(x_0 - x)$ is determined for various pH's of the mixture within the limits of $6 \leq \text{pH} \leq 12$ and at various concentrations of the strontium in the centrifugate. The latter are varied by changing the volume of the active solution containing $^{89}\text{Sr}^{2+}$ introduced into the system within limits ensuring a change in the activity of the centrifugate from 200 to 5000 cpm/ml.

Use the experimental data to find the relation between $\log [x/(x_0 - x)]$ and the pH of an equilibrium solution, and check the possibility of using Eq. (2.5) for describing the coprecipitation of $^{89}\text{Sr}^{2+}$ with $\text{MnO}_2 \cdot \text{H}_2\text{O}$.

Similar experiments can be performed with the system $\text{Fe}(\text{OH})_3\text{-Sr}^{2+}\text{-H}_2\text{O}$, but here the pH of the solution must be brought up to the required value by adding ammonia.

Experiment 2.9.-CAPTURE OF RADIOACTIVE ISOTOPES BY THE PRECIPITATE UPON THE CONSECUTIVE PRECIPITATION OF A MACROCOMPONENT FROM AN AQUEOUS SOLUTION [13]

Upon the partial separation of a macrocomponent into the solid phase, radioactive isotopes having a coefficient of cocrystallization $D \gg 1$ are captured completely by the precipitate already at a small fraction of the precipitated macrocomponent; at $D \ll 1$, the microcomponent does not virtually pass over into the precipitate, while at $D \approx 1$, the fraction of the coprecipitated radioactive isotope increases with an increasing fraction of the precipitated macrocomponent. The distribution laws are studied in this case by using the method of consecutive partial precipitation. It consists in consecutively adding to the system portions of the precipitant sufficient for transferring a small fraction of the macrocomponent into the solid phase, and determining the amount of the radioactive isotope captured upon each consecutive precipitation.

The method of partial coprecipitation can be used, for example, to study the capture of $^{204}\text{Tl}^+$ by precipitates of AgI or PbI_2 .

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. An arrangement for studying consecutive coprecipitation (Fig. 2.6). A magnetic agitator. A water jet pump. A pipette for 1 ml with a syringe. A measuring cylinder for 25 ml.

Radioactive Substances. A solution containing ^{204}Tl with a specific activity of 2×10^4 cpm/ml.

Reagents. Solutions: 0.1 M AgNO_3 ; 0.1 M KI ; 0.1 M Pb .

Performance of Work

Pour 10 ml of 0.1 M solutions of $\text{Pb}(\text{NO}_3)_2$ or 0.1 M AgNO_3 and 1 ml of a solution containing $^{204}\text{Tl}^+$ with an activity of 2×10^4 cpm/ml into the reaction flask of the arrangement for studying partial coprecipitation (Fig. 2.6). Use the water jet pump to suck the solution through a filtering membrane (glass filter No. 3) into a cell where the activity of the initial solution is measured. Force the solution from the cell back into the reaction flask with compressed air.

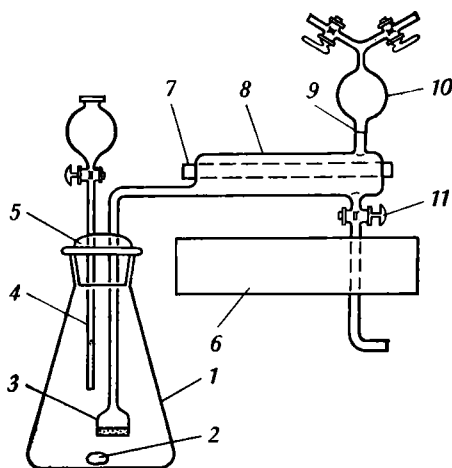


Fig. 2.6.

Arrangement for studying the capture of radioactive isotopes upon the partial precipitation of the macro-component:

1—reaction flask; 2—magnetic agitator; 3—tube for taking samples with a glass filtering membrane (filter No. 3); 4—funnel for pouring in precipitant; 5—ground-glass joint; 6—lead shielding screen; 7—counter of radioactive element radiation; 8—planchet for solution whose activity is being measured; 9—mark showing constant volume of active solution in planchet; 10—buffer vessel; 11—cock

Add 1 ml of an 0.1 *M* solution of KI to the flask, stirring the mixture with the magnetic agitator. In 5-7 min after adding the KI, switch off the agitator and allow the precipitate to settle on the bottom of the flask. Suck the solution twice into the measuring cell and force it back out into the flask for washing the cell. Next fill it with the mother liquor and measure its activity. Now force out the mother liquor into the reaction flask, add a new portion (1 ml) of the KI solution, agitate the mixture, and so on according to the above procedure. Repeat all these operations until the total volume of the poured in KI solution exceeds 15 ml.

Taking into account that during the 5-7 minutes of agitating the mixture after the pouring in of a new portion of KI the supersaturation of the solution created by this portion is completely eliminated, use the reaction equation to calculate the mass of the precipitate after the addition of each

portion and compare it with the relative amount of $^{204}\text{Tl}^+$ coprecipitated by it.

Check the possibility of using Eqs. (2.1) and (2.2) for describing the coprecipitation of $^{204}\text{Tl}^+$ with PbI_2 and with AgI .

Experiment 2.10. SEPARATION OF $^{141}\text{Ce}^{3+}$ WITH AN ISOTOPE CARRIER AND APPRAISAL OF ITS RADIOCHEMICAL PURITY [14]

Preparations of ^{141}Ce may contain radioactive isotopes of lanthanum and barium. The radiochemical purification of the initial preparation can be performed by the method of coprecipitation with an isotope carrier.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β - or γ -radiation. A water bath. Beakers for 150 ml (6). A sectional funnel for filtration. Centrifuge tubes. A washing bottle.

Radioactive Substances. A solution containing $^{141}\text{Ce}^{3+}$ without a carrier, with a specific activity of 1000 cpm/ml, and a similar solution, but contaminated with $^{140}\text{La}^{3+}$ and $^{140}\text{Ba}^{2+}$.

Reagents. Ammonia. Methyl orange (a 0.01% solution). Solutions: 1% $\text{Ce}(\text{NO}_3)_3$, $\text{La}(\text{NO}_3)_3$, and BaCl_2 ; saturated and diluted $\text{C}_2\text{O}_4\text{H}_2$; concentrated HNO_3 ; 0.5 N HCl ; 0.25 M KIO_3 ; 1 N H_2SO_4 , solid $\text{Ce}(\text{NO}_3)_3$, $\text{La}(\text{NO}_3)_3$, BaCl_2 .

Performance of Work

Determine the specific activity of the initial solution of radiochemically pure $^{141}\text{Ce}^{3+}$. To do this, accumulate a definite amount of the solution on the filter, dry it, and measure the activity with a counter.

Appraise the amount of the isotope carrier needed for the most complete extraction of the cerium in the form of an oxalate. For this purpose, pour into each of 6 beakers 1 ml of lanthanum and barium solutions, 5 ml of a solution containing the radiochemically pure radioactive isotope ^{141}Ce , and increasing amounts of a 1% solution of $\text{Ce}(\text{NO}_3)_3$ (0.1, 0.5, 1.0, 2.0, 3.0 and 5.0 min). For the volumes of the solutions to remain the same, add to each beaker the relevant amounts of water (from 4.9 to 0 ml). Heat the solutions

up to 60 °C and add 3 ml of a saturated solution of oxalic acid.

Hold the beakers during one hour on the water bath, after which filter the precipitates, wash them with dilute oxalic acid, dry them, and measure their activity. Plot the activity of the preparations against the amount of the cerium salt taken for precipitation. Calculate for each preparation the yield of the isotope (in %). Use the curve to choose the smallest amount of isotope carrier ensuring the complete extraction of ^{141}Ce from the solution.

Next begin the radiochemical purification of the preparation of $^{141}\text{Ce}^{3+}$ contaminated with $^{140}\text{Ba}^{2+}$ and $^{140}\text{La}^{3+}$.

To 5 ml of the solution of $^{141}\text{Ce}^{3+}$ contaminated with $^{140}\text{Ba}^{2+}$, and $^{140}\text{La}^{3+}$ add the previously found minimum amount of $\text{Ce}(\text{NO}_3)_3$ sufficient for the complete extraction of the $^{141}\text{Ce}^{3+}$, 10 mg each of $\text{La}(\text{NO}_3)_3$ and BaCl_2 , 1 ml of concentrated nitric acid, and boil the solution several minutes. Add ammonia dropwise, and precipitate the cerium hydroxy hydrate, using methyl orange as an indicator. Separate the precipitate from the solution by centrifuging. Preserve the centrifugate. Wash the precipitate with hot water and dissolve it in 0.5 *N* hydrochloric acid. Add 3 ml of a saturated solution of oxalic acid to the acid solution. Centrifuge the cerium oxalate precipitate, wash it with dilute oxalic acid, and again clean it of contaminants. For this purpose, dissolve the precipitate with boiling in concentrated nitric acid and precipitate the cerium in the form of its iodate by adding a 0.25 *M* solution of KIO_3 to the nitric acid solution. Separate the precipitate on the filter of the sectional funnel, wash with a dilute solution of the precipitant and prepare for measuring the activity. Measure the activity of the precipitate during two weeks; determine the half-life of the radioactive isotope in the precipitate, and convince yourself of the purity of the separated ^{141}Ce .

Heat the centrifugate obtained after separation of the cerium hydroxy hydrate to 80 °C and add 2 ml of 10% sulphuric acid to it. Hold the precipitate of BaSO_4 during one hour in the mother liquor, filter it, dry it, and determine its activity. Transfer the filtrate onto a planchet for measuring the activity, evaporate it until dry, and measure the activity. Appraise the content of radiochemical contaminants in the initial preparation.

Experiment 2.11. PRIMARY ADSORPTION OF $^{89}\text{Sr}^{2+}$ BY THE SURFACE OF BaSO_4 CRYSTALS

Barium sulphate is a convenient adsorbent for radioactive isotopes because its stable precipitate has a developed surface and a high sorptivity with respect to small amounts of isomorphous and non-isomorphous contaminants.

The isomorphous salt $^{89}\text{SrSO}_4$ is sorbed by the BaSO_4 precipitate mainly at the expense of primary ion-exchange adsorption so that the transition of the $^{89}\text{Sr}^{2+}$ from the solution to the surface of the stable solid phase of BaSO_4 is unambiguously characterized by the coefficient λ_0 . The object of the present experiment is to determine the coefficient λ_0 for the adsorption system BaSO_4 - $^{89}\text{SrSO}_4$ - H_2O and to find how the adsorptivity of the precipitate depends on its specific surface area.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A shaker. A lamp for evaporation. Test tubes for 10 ml (10). Pipettes for 10 ml. Pipettes for 1 ml (5). Standard bowls for measuring the activity of a liquid for 3 ml (10). A measuring cylinder for 25 ml.

Radioactive Substances. A solution of BaSO_4 saturated at 20°C and containing carrier-free $\text{Na}_2^{89}\text{SO}_4$ with an activity of about 5×10^4 cpm/ml. A solution of BaSO_4 saturated at 20°C containing carrier-free $^{89}\text{Sr}^{2+}$ with an activity of about 5×10^4 cpm/ml.

Reagents. A suspension of BaSO_4 crystals containing 0.1 g of dry mass per ml of solution prepared by pouring together equivalent amounts of solutions of BaSO_4 and Na_2SO_4 with the following decantation washing of the precipitate with water during 6-8 months at room temperature. A suspension of BaSO_4 crystals containing 0.1 g of dry mass per ml of solution, prepared by the decantation washing of the freshly prepared precipitate of BaSO_4 in water at 40, 60, 80, and 100°C during 2-3 months (the thermostating may be interrupted at night). Solutions: BaSO_4 saturated at 20°C and obtained by stirring the precipitate of BaSO_4 washed by decantation in H_2O during one or two days; 1 M HNO_3 .

Performance of Work

Determine the amount of precipitate that should be introduced into the system when studying the primary adsorption of $^{89}\text{Sr}^{2+}$. For this purpose, transfer 1 ml of the initial solution of $^{89}\text{Sr}^{2+}$ and 9 ml of a solution of BaSO_4 saturated at 20°C into each of two test tubes with ground-glass stoppers. Add to the first tube 1 ml of a preliminarily shaken

suspension of BaSO_4 crystals stabilized at room temperature in which the dry mass content is 0.1 g/ml. Add 1 ml of H_2O to the second tube. Close the tubes with their ground-glass stoppers and shake their contents in the shaker during 30 min. Stop the shaking, allow the precipitate added to the first tube to settle on its bottom, and take 1 ml of the liquid phase from each tube. Measure the activity of these samples after first diluting them two times with 1 *N* nitric acid and thoroughly stirring them before the measurement.

Use the results of measuring the activity of the liquid in the first and second tubes to calculate the volume of the suspension that must be added to the system for reducing the activity of the ^{89}Sr in the solution over the precipitate to from one-half to one-third of the initial value. For this purpose, equate the difference between the activities of the solutions in the two tubes to the activity of the adsorbed microcomponent, take into account that $y_0 - y = LV$ (where $L = 2.3 \times 10^6$ g/ml is the solubility of BaSO_4 at 20 °C, and V is the volume of the solution in the tubes, ml), and appraise the parameter $\lambda_0 s l \rho$ by formula (2.6). Next use formula (2.11) to calculate the mass of the precipitate of BaSO_4 and the volume of the suspension that should be added to the system. Introduce the calculated volumes of the suspension into two clean test tubes, add 1 ml of the initial solution of $^{89}\text{Sr}^{2+}$ to one of them, and 1 ml of a solution of $\text{Na}_2^{35}\text{SO}_4$ whose activity I_0 is preliminarily measured to the other one.¹

Bring the volume of the mixtures in both tubes up to 10 ml with a saturated solution of BaSO_4 . Close the tubes with their ground-glass stoppers and shake them in the shaker for 2 hours. Stop the shaking every 20-30 min and (after complete settling of the precipitate to the bottom of the tubes) take 1-ml samples of the solutions. Transfer these samples into bowls for measuring the activity of liquids, to each of which add 1 ml of 1 *M* HNO_3 to prevent adsorption of the radioactive element by the walls of the bowls, and measure the activity I of the samples after stirring them with a glass rod.

Calculate the adsorption factor $x/(x_0 - x) = (I_0 - I)/I$ at the instant of taking each sample, and plot this factor versus the duration of adsorption for $^{89}\text{Sr}^{2+}$ and $^{35}\text{SO}_4^{2-}$. Use the plot to appraise the time needed for the setting in of adsorption equilibrium and the stability of the adsorbent.

Using the equilibrium adsorption factor $x/(x_0 - x)$ for $^{35}\text{SO}_4^{2-}$, calculate the amount (y') of BaSO_4 on the surface of the solid phase by Paneth's formula

$$y' = \frac{x}{x_0 - x} LV$$

Determine the coefficient λ_0 characterizing the equilibrium adsorption of $^{89}\text{Sr}^{2+}$ on the surface of the BaSO_4 precipitate stabilized at room temperature by formula (2.6) with the aid of the data on the adsorption factor $x/(x_0 - x)$ for $^{89}\text{Sr}^{2+}$ and the quantity y' .

Repeat the experiments using suspensions stabilized at 40, 60, 80, and 100 °C. Compare the quantities y' , $x/(x_0 - x)$, and λ_0 for equal masses of precipitates stabilized at different temperatures, and convince yourself that the coefficient of surface cocrystallization is independent of the parameter y' proportional to the specific surface of the adsorbent.

Experiment 2.12. SECONDARY ELECTROSTATIC ADSORPTION OF $^{152}\text{Eu}^{3+}$ ON THE SURFACE OF BaSO_4 CRYSTALS

Secondary electrostatic adsorption can be identified according to its dependence on the concentration of the potential-forming ions. For the adsorption of Eu^{3+} ions on the surface of BaSO_4 crystals, the adsorption increases with an increasing negative charge of the surface associated with the adsorption of the sufficiently well adsorbed potential-forming ions SO_4^{2-} , which is not at all difficult to prove.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of γ - or β -radiation. A centrifuge. A shaker. Flasks for 20-30 ml with a ground-glass stopper (4). Pipettes for 1, 2, and 5 ml with syringes. A cupped planchet for measuring activity for 5 ml. Centrifuge tubes for 10-15 ml (4). A 10-ml measuring cylinder.

Radioactive Substances. A solution containing $^{152}\text{Eu}^{3+}$ (or $^{154}\text{Eu}^{3+}$) with a specific activity of about 5×10^4 cpm/ml and with a concentration of the isotope carrier of not over 10^{-7} M.

Reagents. A stabilized suspension of BaSO_4 containing 0.1 g of BaSO_4 per ml of solution and obtained by pouring together strictly equivalent amounts of $\text{Ba}(\text{NO}_3)_2$ and Na_2SO_4 with the following decantation washing with doubly distilled water during 6-8 months. Solutions: BaSO_4 saturated at 20 °C; 0.2 M K_2SO_4 ; 0.2 M KCl.

Performance of Work

Determine the activity of the initial solution containing $^{152}\text{Eu}^{3+}$. For this purpose, dilute 1 ml of the solution 10 times with a saturated solution of BaSO_4 . Transfer 1 ml from the dilute solution into a standard planchet and measure the activity.

Calculate the volume of the initial solution that would ensure an activity of the solution in the planchet of 2000 cpm.

Transfer the calculated volumes of the initial solution containing $^{152}\text{Eu}^{3+}$ into four flasks with ground-glass stoppers having a capacity of 20-30 ml, and add to each of them 1 ml of an 0.2 *M* solution of K_2SO_4 . Add 1 ml of a stabilized suspension of BaSO_4 to each of three of these flasks.

Next bring the volume of the mixture in all four flasks up to 10 ml with doubly distilled water. Shake the flasks with a precipitate during 20 min in the shaker (until adsorption equilibrium sets in). Remove the flasks from the shaker, transfer the suspensions into the centrifuge test tubes, and centrifuge them for 3-5 min. Take 5 ml of the liquid phase from each of the centrifuge tubes and the fourth flask and transfer the samples consecutively into the planchet, where the activity I_{sln} of the centrifugates and I_0 of the solution from the fourth flask are determined.

Calculate the adsorption factor $x/(x_0 - x) = (I_0 - I_{\text{sln}})/I_{\text{sln}}$ corresponding to the adsorption of Eu^{3+} from a 0.02 *M* solution of K_2SO_4 . Repeat the experiment, varying the amount of the K_2SO_4 solution added to the system from 0.1 to 0.8 ml, and simultaneously adding accordingly from 0.9 to 0.2 ml of a 0.2 *M* solution of KCl (so that the total volume of the introduced solutions of K_2SO_4 and KCl will be 1 ml).

Use the data obtained to plot the factor $x/(x_0 - x)$ versus the logarithm of the concentration of K_2SO_4 in an equilibrium solution. Appraise the value E_0 of the normal potential at the BaSO_4 crystal-solution interface in the conditions of the experiments, using formulas (2.7) and (2.8).

**Experiment 2.13. MOLECULAR ADSORPTION
OF $^{95}\text{Zr}^{\text{IV}}$ FROM HYDROCHLORIC ACID SOLUTIONS
ON FLUOROPLASTIC-4 [15]**

The surface layer of Fluoroplastic-4 (polytetrafluoroethylene) carries no appreciable Coulomb charge, while $^{95}\text{Zr}^{\text{IV}}$ in a hydrochloric acid solution in addition to a multitude of ions forms a large number of neutral molecules having the general formula $\text{Zr}(\text{OH})_x\text{Cl}_{4-x}$, which makes the system fluoroplastic-4- Zr^{IV} a convenient object for studying molecular adsorption.

Equipment and Reagents

Equipment and Utensils. A counter for measuring soft β -radiation. A Warren motor. A thermostat. Fluoroplastic disks with prolongations (8) with an area of 5 cm^2 and a thickness of 1-2 mm. A set of aluminium screens. Pincers. Beakers for 50 ml (8). Beakers for 100 ml (2). A measuring cylinder for 20 ml. Pipettes for 1 ml with syringes.

Radioactive Substances. Solutions containing $^{95}\text{Zr}^{\text{IV}}$ with an activity of about 10^5 cpm/ml and a varying acidity (0.1, 1, 4, 6, 8, 10 N) that before use were left standing for over 24 hours. A hydrochloric acid solution (4 M HCl) held for 24 hours and containing $^{95}\text{Zr}^{\text{IV}}$ with an activity of about 10^7 cpm/ml.

Reagents. Solutions of various normality (from 0.1 to 10); 1 N H_2SO_4 . Benzene.

Performance of Work

Connect a fluoroplastic disk with prolongations preliminarily washed with benzene and water to a Warren motor with the aid of grip (Fig. 2.7). Fasten the motor so that the disk will be in a 50-ml beaker without touching its walls and not reaching the bottom by 1-2 mm. Pour 4 M hydrochloric acid into the beaker until the acid covers the entire disk except for its prolongation. Record the volume of the acid added. Determine how much of the initial active solution of ^{95}Zr must be added to the beaker. For this purpose, transfer a strictly measured volume of the active solution dropwise to a round filter with an area of 5 cm^2 , dry the filter, and measure the activity with an end-window counter using an aluminium screen to completely absorb the radiation of the decay product of ^{95}Zr —Nb.

Use the results of the measurements to calculate the volume of the initial active solution that must be added to the beaker with the disk for the activity of the solution in

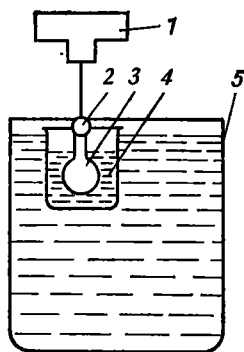


Fig. 2.7. Arrangement for studying adsorption of radioactive elements on a fluoroplastic disk:

1—Warren motor; 2—grip; 3—fluoroplastic disk with prolongation; 4—solution being tested; 5—thermostat

the beaker to be 5×10^3 cpm/ml. Introduce the calculated volume of the active solution into the beaker, vigorously stirring the liquid in the beaker with a glass rod. Switch on the Warren motor for 10 min. Next extract the disk from the beaker, holding it with the pincers by its prolongation, wash it by consecutively immersing it for 1-2 s into two vessels filled with 4 M hydrochloric acid free of radioactivity, dry it, and measure its activity in conditions identical to those for determining the activity of the initial solution of ^{95}Zr . Repeat the immersion of the disk into the active solution and the measurement of the activity of the adsorbed ^{95}Zr four or five times to achieve adsorption equilibrium. Measure the activity of the equilibrium solution. Use formula (2.9) to calculate the equilibrium adsorption coefficient α .

For desorption of the Zr, wash the fluoroplastic disks three times with hot 1 N sulphuric acid and water. Owing to incomplete desorption, measure the background of the disks before each experiment.

In a similar way, determine the coefficient with various amounts of ^{95}Zr in the solution, increasing the activity of the initial solution from 1×10^4 to 4×10^5 cpm/ml, and with various normalities of the hydrochloric acid (from 0.1 to 10 N). The duration of adsorption in each experiment must be sufficient for equilibrium to set in.

At an activity of the initial solution of 1×10^4 cpm/ml and 10 *N* concentration of HCl, determine the temperature dependence of the coefficient α . For this purpose, perform the experiments in a thermostat (see Fig. 2.7) that keeps the temperature at 0, 20, 40, or 60 °C.

Using the experimental data, calculate the adsorption energy of ^{95}Zr (in kJ/mol) by formula (2.10).

Experiment 2.14. ADSORPTION OF $^{32}\text{PO}_4^{3-}$ BY SURFACE OF GLASS [16]

One of the most widespread adsorbents is glass. Its hydrated surface, containing silica-acid groups, can retain the most diverse radioactive isotopes at the expense of primary and secondary adsorption. The adsorption of radioactive isotopes by glass depends on the grade and the preliminary treatment of the glass, and also on the composition of the solution containing a radioactive isotope. This is not difficult to observe, using the example of the capture of ^{32}P by glass in the form of the phosphate ion.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A water bath. Glass plates (with a total area of 6 cm²) made from various grades of glass (heat-resistant, quartz, neutral, white No. 23, etc.). A pH meter. Pincers. Beakers for 50 ml (5).

Radioactive Substances. A solution of $\text{Na}_3^{32}\text{PO}_4$ (pH = 8) with an activity of about 10^7 cpm/ml.

Reagents. Benzene. Acetone. Solutions: 2 *N* NaOH; 2 *N* and concentrated H_2SO_4 ; 2 *N* H_3PO_4 .

Performance of Work

Place a plate of a definite grade of glass degreased with benzene and washed with water into a 50-ml beaker, pour in a 2 *N* solution of NaOH and heat on the water bath during 10 min. Extract the plate from the alkali, wash it with water and acetone, dry it, and transfer it into a 50-ml beaker filled with 40 ml of an $\text{Na}_3^{32}\text{PO}_4$ solution with an activity of 10^7 cpm/ml, and hold it there for 10 min. Extract the plate from the active solution with the pincers, consecutively immerse it for 2–4 s into three 50-ml beakers filled with distilled

water, dry it in the air, and measure the activity of the adsorbed $^{32}\text{PO}_4^{3-}$.

Repeat the experiment, varying the duration of treatment of the plate with the alkaline solution (from 1 min to 2 h), the grade of glass, and the pH of the solution containing the ^{32}P ($12 > \text{pH} > 8$). The latter is done by adding H_3PO_4 to the solution.

In a similar way, study the adsorption of ^{32}P by glass preliminarily treated in $2\text{ N H}_2\text{SO}_4$.

Wash the plates with concentrated sulphuric acid up to complete desorption of the $^{32}\text{PO}_4^{3-}$.

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Chapter 3 Chromatographic Methods in Radiochemistry

THEORETICAL INTRODUCTION

The term "chromatography" is commonly applied to the separation of mixtures of gases, vapours, liquids, or solutes by sorption methods. As a rule, separation is performed in dynamic conditions, i.e. by passing the mixture of substances to be separated through a column filled with a sorbent. This is attended by multifold alternation of elementary events of sorption-desorption, which increases the degree of separation of substances even when the differences in the force of interaction of each of them with the sorbent are small. Hence, chromatographic methods can be used to separate components that are close in their properties.

Chromatographic methods are classified according to the following features:

(a) according to the state of aggregation of the system in which separation is being performed, we distinguish **gas**, **gas-liquid**, and **liquid** (liquid-liquid and liquid-solid) chromatography;

(b) according to the mechanism of separation, we distinguish **molecular** (adsorption), **partition**, **ion-exchange**, and **deposition** chromatography;

(c) according to the way of performing the process, we distinguish **column**, **capillary**, and **surface** (paper and thin layer) chromatography.

Three variants of performing a dynamic (column) process of separating substances are distinguished, in turn: **frontal analysis**, **displacement chromatographic analysis**, and **elution** (developing or washing) analysis.

Frontal analysis is performed by continuously passing a mixture of the substances being separated through a column with a sorbent. In the displacement and elution methods, the mixture to be separated into components is first introduced into the upper part of the column, and separation is performed in the **displacement** method by a reagent that is sorbed on the given sorbent better than any

other components of the mixture, and in the **elution method** either by a pure solvent or by a solution of a substance that is sorbed the least by the given sorbent.

Let us briefly characterize the main kinds of chromatography proceeding from the classification according to the mechanism of the process.

In **molecular (adsorption) chromatography**, the differences between the intermolecular forces acting between the individual components of the mixture being separated and the adsorbent are used for separation.

In **partition chromatography**, use is made of the differences in the distribution of substances between two liquid phases—immiscible solvents, one of which is a stationary phase on the adsorbent, and the other is a mobile phase. Paper chromatography (see below) is a variant of partition chromatography.

The method of **deposition chromatography** is based on the differences in the solubility of sparingly soluble precipitates formed as a result of a chemical reaction between the ions being chromatographed and the precipitant on the adsorbent in the column.

Ion-exchange chromatography is based on the differences in the distribution of ions between a solution and a sorbent that are capable of exchanging ions.

In accordance with the content of the experiments to be run, in the following we shall consider the basic laws of ion-exchange, paper, and gas chromatography.

A. ION-EXCHANGE CHROMATOGRAPHY [1-4]

Here, ion exchangers are used as sorbents. They are substances containing cations or anions capable of being exchanged in a solution for other cations or anions. Hence, ion-exchange chromatography is based on the difference between the ion exchange equilibrium constants (exchange constants) for the solution and the ion exchanger.

Ion Exchangers

Synthetic high-polymer organic substances—ion-exchange resins—have found the greatest favour as ion exchangers in ion-exchange chromatography. Their most important merits include the substantial (in comparison with other sorbents)

exchange capacity or absorptivity, the stability to acids, alkalis, and, to a somewhat smaller extent, to oxidizing agents, and the almost complete insolubility in water and in most organic solvents. A shortcoming of organic ion exchangers is their comparatively low stability under large radiation doses. Inorganic ion exchangers such as synthetic aluminosilicates—*zeolites*, and zirconium phosphates are more stable to radiation.

The backbone of the most important ion-exchange resins is a product of copolymerization of styrene with divinylbenzene (DVB). This is what we call the **matrix** (support) of the resin. The higher the content of DVB responsible for cross-linking between the linear chains of the styrene polymer, the more "rigid" is the structure of the copolymer, and the lower is its ability to stretch upon the absorption of a solvent. Simultaneously with the synthesis of the copolymer or later, functional groups are introduced into it. These contain ions capable of exchange with the ions from the solution. An ion exchanger containing the functional (in other words—exchange) groups SO_3H , COOH , or OH has the properties of a **cation exchanger**. The presence of the groups $\text{N}(\text{CH}_3)_3$, $\text{NH}(\text{CH}_3)_2$, or NH_2CH_3 imparts properties of an **anion exchanger** to the copolymer.

The ability of an ion exchanger to exchange is determined by the degree of dissociation of the exchange groups that depends on both the chemical nature of the groups and on the properties of the solution. For example, cation exchangers containing only COOH groups dissociate only slightly in an acid medium, and they belong to the category of weakly acidic cation exchangers. The latter are capable of exchange reactions only in a neutral or alkaline medium. Conversely, cation exchangers containing only the SO_3H group are strongly acidic. They are universal because they are capable of exchange in any media (cation exchangers of grades KU-2, KU-23, Dowex-50, AG-1, etc.). Similarly, weakly basic and strongly basic anion exchangers are distinguished. Particularly, the category of strongly basic anion exchangers includes ones containing groups of a quaternary ammonium base (anion exchangers of grades AV-17, Dowex-1, IRA-400, etc.). Polyfunctional ion exchangers containing both strongly acidic (strongly basic) and weakly acidic (weakly basic) exchange groups are called moderately acidic (moderately basic) ion exchangers.

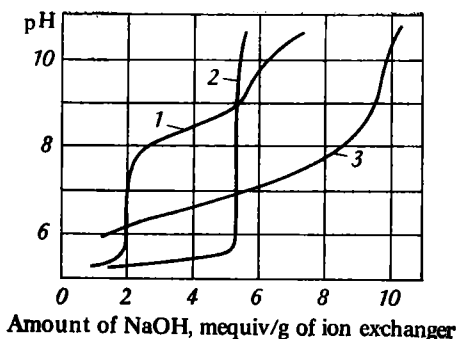


Fig. 3.1. Ion exchanger titration curves:
1—polyfunctional cation exchanger; 2—strongly acidic cation exchanger; 3—weakly acidic cation exchanger

The most important characteristics of ion exchangers are their exchange capacity and swelling capacity.

The **exchange capacity** is a measure of the ability of an ion exchanger to absorb ions from a solution. The **total exchange capacity of an ion exchanger (TEC)** is determined by the maximum number of milliequivalents of the ions that can be absorbed by 1 g of a dry-weight ion exchanger taken in the hydrogen (cation exchanger) or chloride (anion exchanger) form*. The TEC of ion exchangers is determined by their content of exchangeable groups and approximately equals several mequiv per gramme of ion exchanger. For example, the TEC of the cation exchanger of grade KU-2—one of the most widely used Soviet cation exchangers—is about 5 mequiv/g of dry-weight exchanger.

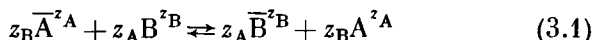
The capacity of ion exchangers is determined in various ways (see Experiment 3.1). Most often, potentiometric titration is used. A cation exchanger in the H form is titrated with a solution of an alkali (Fig. 3.1), an anion exchanger in the OH form—with a solution of an acid. We must note that the capacity of weakly acidic cation exchangers (or weakly basic anion exchangers), unlike that of strongly acidic cation exchangers (strongly basic anion exchangers) depends greatly on the pH of the solution (curve 3 in Fig. 3.1).

* To transfer an ion exchanger into an ionic form, it is treated with a solution of the given ion up to saturation.

The **swelling capacity** characterizes the change in the specific volume of an ion exchanger when it is immersed into a solution (and also when the composition and concentration of the solution change). The swelling of an ion exchanger is due to solvation of its lyophilic exchangeable groups. Swelling causes stretching of the elastic matrix of an ion exchanger; owing to the presence of cross links, a force appears in the matrix that prevents its stretching. A quantitative measure of this force is the **swelling pressure** π . The latter equals the difference between the osmotic pressure of the solution in the pores of the ion exchanger and the external solution. The swelling pressure grows with an increase in the capacity and degree of cross linking of the ion exchanger, upon the replacement of the multicharged counterions (i.e. the exchange ions of the functional group) with ions having a smaller charge, upon an increase in the degree of solvation of the ions, and upon lowering of the concentration of the solution.

Equilibrium of Ion Exchange

Let us consider a system containing an ion exchanger and a solution in which counterions A with a charge of z_A and counterions B with a charge of z_B are present. The exchange of ions A and B between the ion exchanger and the solution follows the equation



(a bar capping a symbol here and below signifies components relating to the ion exchanger phase).

The thermodynamic equilibrium constant of the ion exchange reaction (3.1) K_{th} is

$$K_{th} = \frac{\bar{a}_B^{z_A} \bar{a}_A^{z_B}}{\bar{a}_A^{z_B} \bar{a}_B^{z_A}} \quad (3.2)$$

where a_A and a_B are the thermodynamic activities of the relevant ions. Grouping the terms relating to the solution on the right-hand side, those relating to the ion exchanger on

the left-hand side, and raising both sides of Eq. (3.2) to the power $1/(z_A z_B)$, we obtain

$$\frac{a_B^{1/z_B}}{a_A^{1/z_A}} = K'_{th} \frac{a_B^{1/z_B}}{a_A^{1/z_A}} \quad (3.3)$$

where $K'_{th} = K_{th}^{1/z_A z_B}$.

For dilute solutions, we may use the concentrations of the exchanging ions in the solution instead of the activities because the activity coefficients equal unity. We may also use the concentrations instead of the activities in the ion exchanger phase if we assume that the ratio of the activity coefficients of the ions raised to powers corresponding to the reciprocals of the charge is a constant quantity. Hence, substituting the concentrations for the activities in Eq. (3.3), we obtain what is known as **B. Nikolsky's equation of the ion exchange isotherm**:

$$\frac{\bar{c}_B^{-1/z_B}}{\bar{c}_A^{-1/z_A}} = K_B^A \frac{c_B^{1/z_B}}{c_A^{1/z_A}} \quad (3.4)$$

where K_B^A is the concentration constant of ion exchange, or the "selectivity coefficient".

A glance at Eq. (3.4) reveals that the plot of $\bar{c}^{-1/z_B}/\bar{c}^{-1/z_A}$ versus $c_B^{1/z_B}/c_A^{1/z_A}$ is a straight line whose slope equals the selectivity coefficient K_B^A . If $K_B^A > 1$, an ion exchanger preferably absorbs ions of B, and if $K_B^A < 1$, it absorbs ions of A.

The theory of ion exchange leads to the following relation between the selectivity coefficient K_B^A , the magnitude of the swelling pressure π , the ratio of the thermodynamic activity coefficients of the ions being exchanged in the ion exchanger phase $\bar{f}$ and in the solution f , the difference of the equivalent volumes of the ions $z_A \tilde{V}_B - z_B \tilde{V}_A$ ($\tilde{V}$ is the partial molar volume of an ion), and the absolute temperature T :

$$\ln K_B^A = \ln \frac{\bar{f}_B^{z_A}}{\bar{f}_A^{z_B}} + \ln \frac{f_A^{z_B}}{f_B^{z_A}} + \frac{\pi}{RT} (z_A \tilde{V}_B - z_B \tilde{V}_A) \quad (3.5)$$

An analysis of Eq. (3.5) allows us to see how different factors affect the selectivity of an ion exchanger with respect to the ions being exchanged. Let us briefly formulate the conclusions obtained that form the basic laws of the selectivity of ion exchange:

1. An ion exchanger in equilibrium with a dilute solution preferably absorbs counterions with a larger charge.

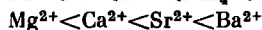
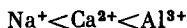
2. With equal charges, an ion exchanger preferably absorbs counterions with a lower effective radius in the solvated state.

3. The selectivity exchange increases with a growth in the capacity and number of cross links in the ion exchanger, with a decrease in the concentration of the solution, and with lowering of the temperature.

4. An increase in the difference between the effective radii of the ions being exchanged in the solvated state facilitates an increase in the selectivity.

The above laws hold for dilute aqueous solutions and for exchange processes not made complicated by complexing, hydrolysis, and other phenomena. With a view to the above, ions can be arranged in what is known as **affinity series**—in the order of the growth in their sorbability on ion exchangers.

Cation exchangers:



Anion exchangers:



etc.

The ion exchange isotherms described by Eq. (3.4) can be depicted graphically, laying off along the coordinate axes the equivalent fractions of the ion B being exchanged in the ion exchanger phase and in the phase of the solution. Now all cases of exchange can be reduced to isotherms of three kinds (Fig. 3.2): **convex** (corresponding to the preferable sorption of the ion B), **concave** (corresponding to the preferable sorption of the ion A), and **linear** (corresponding to the absence of selectivity in exchange).

To characterize the selectivity of ion exchange, in addition to the selectivity coefficient, use is also made of the **distribution** or **partition coefficient** determined directly

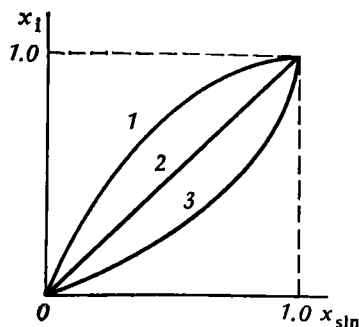


Fig. 3.2.

Ion exchanger isotherms:

1—convex; 2—linear; 3—concave; x_i and x_{sin} = concentration of substance being distributed (in equivalent fractions) in the ion exchanger and solution phases

from experimental data. By definition, the distribution coefficient K_d equals the ratio of the equilibrium concentrations of the ion being studied in the ion exchanger and in the solution. For the distribution coefficient for the ion B, we obtain from Eq. (3.4):

$$K_d = \frac{\bar{c}_B}{c_B} = (K_B^A)^{z_B} \left(\frac{\bar{c}_A}{c_A} \right)^{z_B/z_A} \quad (3.6)$$

If B is a microcomponent (for example, a radioactive isotope), we may disregard the change as a result of the exchange of the macroconcentrations of the ion A in the phase of the ion exchanger and in the solution, i.e. here K_d is a constant quantity proportional to the selectivity coefficient K_B^A . Hence, the selectivity of exchange can be studied by comparing the values of K_d for different ions. The use of radioactive isotopes substantially simplifies the procedure of determining the values of K_d . For calculations in this case, we use the formula

$$K_d = \frac{I_0 - I}{I} \frac{V}{m} \quad (3.7)$$

where I_0 and I are the initial and equilibrium radioactivities of a solution (or its aliquot), V is the volume of the solution, and m is the mass of the dry-weight ion exchanger.

The ratio of the distribution coefficients for two elements in the general case characterizes the degree of their separa-

tion and is known as the **separation factor** K_s . Investigation of how the values of K_d and K_s depend on a variety of factors is used in finding the optimal conditions for the chromatographic separation of ions.

Two ways are used most frequently for increasing the degree of separation of substances: the employment of reagents forming complex compounds with the ions being chromatographed (or with part of them), or the substitution of an organic solvent for the water in the solution. The use of complexing agents is especially effective when separating elements close in their properties (rare-earth elements, actinides, etc.), since the differences in the ion-exchange selectivity of the complex forms of elements are higher than for ions forming no complexes. The replacement of all or part of the water in a solution with an organic solvent miscible with it simultaneously affects many factors causing ion-exchange equilibrium (swelling of the ion exchanger, the degree of solvation of the ions in both phases, the dissociation and association of compounds, etc.) and is used successfully for improving the selectivity in the ion-exchange separation of many elements.

Kinetics of Ion Exchange

The total rate of an ion exchange process on an ion exchanger is determined by one of two main steps: either by diffusion of the ions through the "film" adhering to a grain of the ion exchanger (film, or external diffusion kinetics) or by diffusion inside a grain (gel or internal diffusion kinetics). The conditions of performing a chromatographic process are chosen so that the rate of equilibrium establishment is determined by the faster step—film kinetics. The predomination of film kinetics is facilitated by the following factors: a small grain size, a high capacity and a low degree of cross linking of the ion exchanger, a low concentration of the solution, and a low speed of its flow through the ion exchanger layer.

Dynamics of Ion Exchange

The replacement of counterion A in the exchange group of an ion exchanger with another ion B is an example of the simplest ion-exchange process. In the static method of

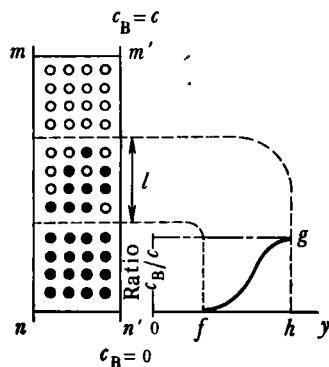


Fig. 3.3.

Schematic view of separation of A and B ions in a column with an ion exchanger:

black circles—ion exchanger in form RA; white circles—ditto, RB; mm' —upper boundary, and nn' —lower boundary of layer of ion exchanger; l —width of exchange zone; fg —front of migration of ion B; h —point corresponding to achievement of maximum concentration of B in eluate

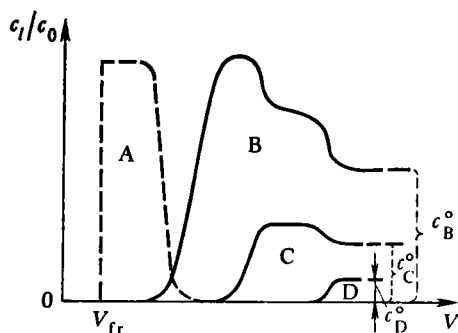


Fig. 3.4.

Elution curves in separating ions A, B, C and D by frontal chromatography (c_i/c_0 = relative concentration of ion in eluate; V = volume of eluate)

exchange (batch separation), the task is solved by multi-fold renewal of the portions of the solution containing the ion B and in contact with the ion exchanger in the form RA (see Experiment 3.2). It is much simpler to replace the ion A with B in an ion exchanger by using the dynamic method (column separation) in which a solution containing the ion B is continuously passed through a column filled

with the preliminarily swollen ion exchanger in the form RA. As the solution travels along the column, its first portions that have passed through the upper layers of the exchanger and are already lean in ions B encounter layers of the exchanger that are richer in ions A; at the same time the upper layers of the ion exchanger lean in ions A come into contact with fresh portions of the solution rich in B ions, and so on. Hence, along the entire path of the solution through the column, the ion-exchange equilibrium continuously shifts in the direction of a greater absorption of B ions by the ion exchanger. At a definite instant after the beginning of the process, the upper layers of the exchanger completely pass over into the form RB, whereas the lower layers still remain in the form RA. In the intermediate part of the column, both the ion exchanger and the solution contain A and B ions. This section of the column is called the **exchange zone** (Fig. 3.3). The composition of the solution in the exchange zone depends on the distance travelled by the solution in the ion exchanger layer. The ratio of the concentration of ion B in the solution c_B to its total concentration c as a function of the distance along the column axis from the top boundary of the ion exchanger layer is illustrated in the right-hand side of Fig. 3.3. Curve *fg* characterizes the **front** of migration of the ion being exchanged along the column. A narrower exchange zone results in a steeper front of migration of the relevant ion, and in a shorter time from the appearance of the ion B in a definite section of the column below the exchange zone up to its achieving the maximum concentration in this section. We can plot a curve similar to curve *fg* by plotting the relative (or absolute) concentrations of the ion at the end of the column along the axis of ordinates and the volume of the passed solution (or the time from the beginning of the experiment) along the axis of abscissas. We obtain what is called an **elution curve**. Its arrangement and shape depend on both the static (distribution coefficient) and the kinetic characteristics of the ion-exchange process, and also on how it is conducted—using frontal, displacement, or elution analysis.

Frontal Analysis. A solution containing a mixture of ions B, C, and D is passed through a column with an ion exchanger in the form RA. The selectivity series of the ions is $A < B < C < D$. In this case, the elution curves of the

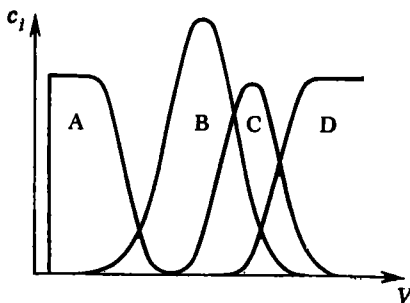


Fig. 3.5. Elution curves in separating ions A, B, C, and D by displacement analysis (c_i = concentration of ion in eluate, V = volume of solution)

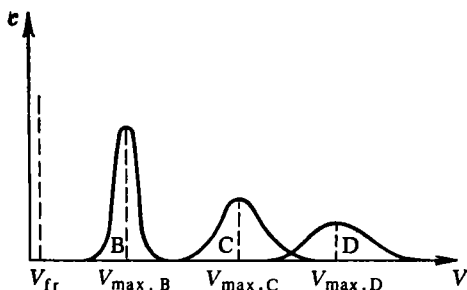


Fig. 3.6. Elution curves in separating a mixture of ions B, C, and D by elution analysis (c = concentration of ion in eluate, V = volume of eluate, V_{fr} = free volume of column, V_{max} = volume corresponding to the maximum concentration of an ion in the eluate)

ions (the **chromatogram** of the mixture) have the form shown in Fig. 3.4.

Examination of the figure reveals that frontal analysis allows one to separate only one ion in the pure form from a mixture—the one that is sorbed the least. Being poorly suitable for quantitative separations, however, frontal analysis is used successfully as an express method in solving a number of problems: the demineralization of waters, the concentration of a sum of microimpurities, the determination of the number of components in a mixture of substances difficult to separate, etc.

Displacement Analysis. In this method, as in elution analysis, the mixture of ions to be separated is prelim-

inarily sorbed in a small volume at the top of the column, and then the washing solution (eluent) is passed through. In displacement analysis (let the ion exchanger have the form RA, the mixture of ions B, C and D is to be separated, and the selectivity series is as above), the column is washed with a solution containing the ion E that is sorbed to a *higher* degree than all the other ions in the mixture. The elution curves have the form shown in Fig. 3.5.

The exchange zones follow one another, travelling along the column at identical speeds depending on the speed of flowing of the solution through the column, the concentration of ion E, and the capacity of the ion exchanger.

Displacement analysis makes it possible to obtain pure fractions of the components, but the quantitative separation of ions with a close selectivity is hampered owing to overlapping of the curves.

Elution Analysis. In this method of chromatography, unlike displacement analysis, the column with the sorbed ions is washed (eluted) with a solution containing ions having the *lowest* affinity to the ion exchanger (for example, ions A). The elution curves in elution analysis have the form shown in Fig. 3.6.

It is important that the exchange zones travel at different speeds in elution analysis. By varying the length of the column, the concentration, the speed of passing the eluent, and other factors, one can achieve in principle separation of the elution curves for elements that are neighbours in the selectivity series.

We must note that in elution analysis, $V_{\max}$ —the volume of the solution corresponding to a peak of the elution curve—is related to the distribution coefficient K_d by the simple expression $K_d = (V_{\max} - V_{fr})/m$, where m is the mass of the ion exchanger, and V_{fr} is the free volume of the column, i.e. the volume occupied by the liquid in the column between the particles of the swollen ion exchanger*.

*

The free volume of a column is the difference between the volume occupied by the ion exchanger together with the eluent and that occupied by the exchanger alone. It is simple to find the free volume experimentally, for example, by using a radioactive indicator not absorbed by the given exchanger. The free volume of the column in this case equals the volume of the solution that has passed through the

Hence, knowing K_d , we can predict the position of the peak on the elution curve, and vice versa.

Upon considering the shapes of the elution curves for different ways of performing a chromatographic process, one can easily see that the effectiveness of separating ions having an adjacent selectivity depends on two factors: the distance between the peaks of the elution curves (equivalent to the separation coefficient) and the width of the relevant peaks. The influence of various factors on the ion-exchange selectivity, i.e. on the distribution and separation coefficients of the ions, was treated on an earlier page. The width of the elution peaks is affected both by kinetic, hydrodynamic, and other factors, and by how an ion-exchange process is performed.

A quantitative treatment of the dynamics of ion exchange for the case when the kinetics of the process may not be considered (exchange is instantaneous—what is called “equilibrium dynamics”) leads to the following relation between the speed of travelling of a point on the front v_f , the speed of flowing of the solution through the column v , and the first derivative of the sorption isotherm da/dc :

$$v_f = \frac{v}{1 + (da/dc)} \quad (3.8)$$

An analysis of Eq. (3.8) allows us to explain the influence of the form of the sorption isotherm on the nature of travelling of the front of the relevant ion.

According to (3.8), at a constant v , the speed of a point on the front is determined by the derivative da/dc , i.e. by the slope of a tangent to the given point of the isotherm.

When the isotherm is linear, $da/dc = a/c = K_d$ (const), i.e.: (a) all the points of the front travel at a constant speed (“parallel transfer” of the front occurs, see Fig. 3.7a); (b) the larger the distribution coefficient of an ion, the more slowly does its front travel along the column. The last conclusion underlies the method of ion-exchange chromatography.

column with the ion exchanger up to the appearance of radioactivity in the filtrate.

Sometimes elution curves are plotted by laying off quantities along the axis of abscissas that are proportional to the free volume of the column. With such a construction, the position of the elution peak for a definite element does not depend on the column dimensions.

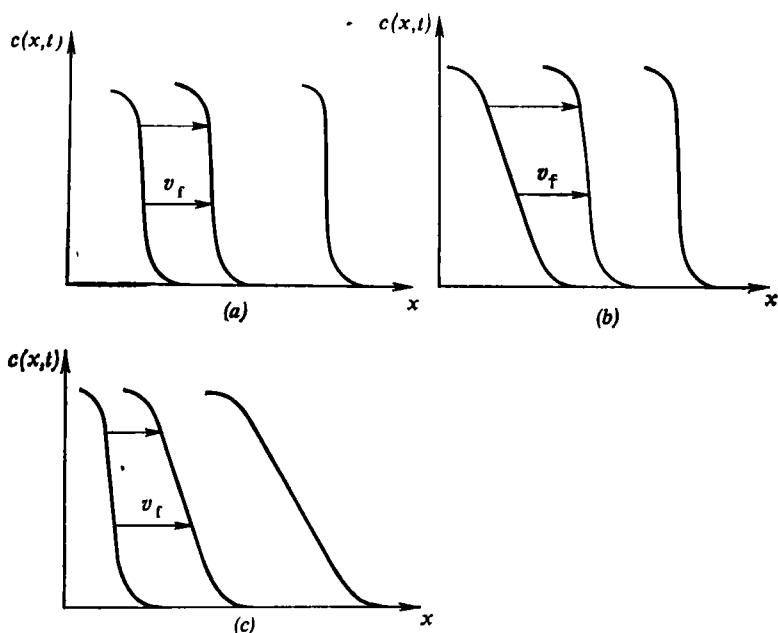


Fig. 3.7. Nature of travel of ion front depending on the kind of exchange isotherm:
a—linear isotherm; *b*—convex isotherm; *c*—concave isotherm;
 $c(x, t)$ = concentration of eluted ion, x = distance from top boundary of ion exchanger layer; v_f = speed of front points

With a convex sorption isotherm, a growth in the concentration is attended by falling off of the quantity da/dc ; hence, points of the front with a higher concentration travel faster, and self-sharpening of the front occurs (Fig. 3.7*b*). A convex isotherm is realized when displacement analysis is used for a process.

With a concave isotherm (elution chromatography), points of the front having a higher concentration travel at lower speeds, and as they travel along the column, the front acquires a gentler slope, becomes "blurred" (Fig. 3.7*c*, see also Fig. 3.6).

In practical ion-exchange chromatography, the mechanism of "non-equilibrium dynamics" is most often realized, when the shape of the elution curves is affected by kinetic

and other factors. With a linear isotherm, and also with a concave one, regular blurring of the front (broadening of the exchange zones) occurs as the front travels along the column with the ion exchanger, while with a convex isotherm what we call a "stationary" front forms beginning from the instant when the narrowing of the front due to the mechanism of the process and its broadening due to kinetic and other factors balance each other.

Hence, deviation of the conditions of performing a chromatographic process from equilibrium ones in all cases leads to "broadening of the peaks" and, consequently, to a lower purity of separation. The practical recommendations on the choice of the ion exchanger (finely dispersed specimens with a high exchange capacity and a low degree of cross linking are preferred) and on the controllable parameters of the process (a low speed of the solution through the column, in some cases elevation of the temperature, etc.) are aimed at bringing the conditions of performing a process closer to the equilibrium ones.

In concluding, we shall note a few advantages of using radioactive isotopes in chromatography. We showed above how the use of isotopes facilitates the determination of the distribution coefficients. Further, if one of two ions being exchanged is present in a microconcentration, we may consider that the exchange follows a linear isotherm, and this simplifies many quantitative calculations. The use of isotopes makes it possible to automate the separation processes, for example by continuous registration of the activity of the eluate leaving a column with the aid of a recording potentiometer.

B. PAPER CHROMATOGRAPHY [1, 5, 6]

Paper chromatography can be considered as a particular case of partition chromatography in which special filter paper is used as the carrier adsorbent, and water sorbed by the cellulose fibres is the stationary phase.

When separating substances by paper chromatography, the solution containing the mixture of components being studied is applied in the form of separate drops on the **starting line**, which is at a distance of 3-4 cm from the edge of the strip of chromatographic paper. After being dried, this edge is immersed in the relevant solvent poured onto the bottom of

the chromatographic chamber. The starting line must be somewhat higher than the surface of the solvent. The solvents used include polar organic liquids (aliphatic alcohols and ketones with a low molecular mass, ethers, and also chloroform, tributylphosphate, etc.) and mixtures of solvents preliminarily saturated with water and an organic or mineral acid.

In a tightly closed chromatographic chamber whose atmosphere is saturated with the solvent vapour, the solvent under the action of capillary forces rises along the paper sheet*. As soon as the solvent reaches the starting line, the components of the mixture being separated are redistributed between the mobile and the stationary phases in accordance with the distribution coefficients of each component. As a result, the mixture is divided into separate zones travelling at different rates together with the solvent. After a definite time depending on the rate of migration of the solvent front, the paper is extracted from the chromatographic chamber and dried. Next the location of the zones of the separate substances is determined by processing the paper with specially selected reagents playing the role of **developers**. In the chromatographic separation of a mixture of radioactive substances, their location is determined in a simpler way, for example by measuring the radioactivity of the dried radiochromatogram along the migration of the solvent front.

The ratio of the rate of travelling of the zone of a substance to the rate of solvent front migration is a constant quantity for given conditions (solvent, temperature) and is known as the R_f parameter. To find R_f , we must measure the distances travelled by the zone of the given substance and by the solvent. It is considered that two substances characterized by the parameters R_f' and R_f'' can be separated if $R_f' - R_f'' \geq 0.1$.

Paper chromatography is customarily used to separate substances in amounts not exceeding 60-80 μg . For radioactive substances, this corresponds to an activity of 37 GBq (1 Ci) without a carrier. After separation, a radioactive

* The vessel with the solvent can be arranged above the sheet of paper; the chromatogram obtained in this case is called **descending**, unlike the **ascending chromatogram** being described.

substance can be recovered by extraction or in some other way.

If a complex mixture of substances is not completely separated in one solvent, separation is repeated in another solvent. One may sometimes succeed in separating a large number of substances simultaneously in this way.

When substances separated by paper chromatography have to be identified, known substances are chromatographed together with the mixture being analysed, and either the positions of the zones (spots) of the substances being analysed and of the standard ones are compared, or the corresponding values of R_f .

Thin-layer chromatography is similar to paper chromatography in the way it is performed. Separations are carried out in a thin (0.1-0.5 mm) layer of a carrier applied to a glass plate or polymer film. A variety of sorbents may be used as the carrier, such as aluminium oxide, activated carbon, silica gel, ion-exchange resins and inorganic ion exchangers. Depending on the task in hand and the chosen sorbent, the principles of partition, ion-exchange, or other kinds of chromatography can be used for separation. In comparison with paper chromatography, separation in a thin layer is considerably faster in the majority of cases.

C. GAS CHROMATOGRAPHY [7, 8]

Gas chromatography is based on the migration of discrete zones of components of a gas or vapour mixture in a stream of a mobile gas phase (called the **carrier gas**) along a layer of a stationary sorbent. In **gas-adsorption** (or **gas-solid**) chromatography, a solid adsorbent is the stationary phase, and in gas-liquid chromatography—a liquid applied to a solid support. Adsorption is the elementary event in gas-solid chromatography, and distribution between the gas phase and the liquid—in gas-liquid chromatography. Separation is due to multifold repetition of elementary events of dissolution, sorption, and desorption. There is a number of intermediate variants, for example, chromatography on a solid sorbent wetted with a small amount of liquid, when the separation processes are determined simultaneously by adsorption on the gas-solid and liquid-solid surface, and also by solubility. In capillary chromatography, the role

of the solid phase is played by the walls of the capillary columns.

In gas chromatography, one determines the content of the vapour of the components in the carrier gas. This underlies the design features of gas chromatographs and their detectors. Depending on whether the total amount of sorbate eluted from the beginning of an experiment or the concentration of the individual components is registered, we distinguish **integral** and **differential** detectors. Differential detectors whose signal is determined by the instantaneous concentration c (in g/cm^3) are called **concentration** ones. If the signal is determined by the mass of the substance in the volume of the detector in unit time (in g/min), the detector is called a **flow** one. The basic parameters of detectors are their **sensitivity** and **inertia**. The latter is measured by the constant τ_0 —the time between the instant when a sample enters the detector and that when a signal is obtained corresponding to 63.2% of the maximum one. A high inertia is a possible cause of peak asymmetry. Differential detectors have a relatively low inertia. For concentration detectors, the sensitivity B [in $(\text{mV} \cdot \text{cm}^3)/\text{mg}$] can be calculated by the formula

$$B = \frac{sv_v}{B_r v q} \quad (3.9)$$

where s is the area of a peak, cm^2 , v_v is the volume rate of flow of the carrier gas, cm^3/min , B_r is the sensitivity of the registering device, cm/mV , v is the speed of the tape, cm/min , and q is the mass of the sample, mg .

The minimum registered concentration $c_{\min}$ (in mg/cm^3) determined by the sensitivity and the noise level m (in mV) is evaluated by the formula

$$c_{\min} = \frac{2m}{B}$$

For flow detectors, the sensitivity $B_{\min}$ [in $(\text{mV} \cdot \text{min})/\text{mg}$] and the minimum registered flow $P_{\min}$ (in mg/min) are:

$$B_{\min} = \frac{s}{B_r v q} \quad P_{\min} = \frac{2m}{B_{\min}}$$

Detection is based on the measurement of various quantities, for example, the heat of combustion of the eluent (thermochemical detectors), the difference between the den-

sities of the eluate and eluent (densimeters), and the difference between their thermal conductivities (katharometers); for the corresponding concentration detectors, $c_{\min}$ ranges from 10^{-3} to 10^{-6} mg/ml. The sensitivity of a number of flow detectors is considerably higher. For example, for a flame-ionization detector when measuring the ionization current of the flame in which the eluate is burned, $P_{\min}$ ranges from 10^{-9} to 10^{-12} mg/min. The minimum flows of the order of 10^{-11} mg/min are registered in radioionization, particularly in argon and electron-capture detectors. The signal of radioionization detectors depends on the content of the eluate in whose presence the mobilities of the charges change, and also on the cross sections of the ionization and recombination processes initiated in the gas flow under the action of the nuclear radiation of an external radioactive source (^{147}Pm , ^{90}Sr , ^3H , ^{63}Ni , ^{85}Kr , ^{226}Ra). When working with labelled substances, of special significance is detection according to the intrinsic radioactivity. This method is characterized by a high sensitivity and a linear relation between the magnitude of the signal and the amount of a component within a broad interval of concentrations; in combination with other methods, it makes it possible to determine the specific activities of the components. Geiger-Mueller counters, proportional and scintillation counters, ionization chambers, etc. can be used as signal transmitters for radioactive components.

The basic elution characteristics determined from differential chromatograms include the retention distances l (in cm) and the corresponding volumes V_{ret} (in cm^3) and retention time t_{ret} (in min). The last two quantities are related to each other by the expression

$$V_{\text{ret}} = t_{\text{ret}} v_v = V_{\text{fl}} \frac{p_0 - p_{\text{lg}}}{p_0} \frac{T}{T_{\text{fl}}} t_{\text{ret}} \quad (3.10)$$

where v_v is the volume rate of flow of the carrier gas, V_{fl} is the reading of the flow meter, p_0 is the pressure at the outlet from the column, p_{lg} is the pressure of the liquid's vapour at T_{fl} , and T_{fl} and T are the temperatures of the flow meter and the column, respectively.

The retention time depends on the column length L , the linear speed α of the carrier gas, and the distribution coefficient

ient Γ_0 of the sorbate between the mobile and stationary phases:

$$t_{\text{ret}} = \frac{L}{\alpha} \Gamma_0 = \frac{L}{\alpha} \frac{a_0}{c_0} \quad (3.11)$$

where $\alpha = v_v/s$, s is the cross-sectional area of the column, a_0 is the mass of a component per unit of column volume, and c_0 is its concentration in the gas phase.

Non-sorbing gases are characterized by the parameters l_0 , V_0 , and t_0 . The differences $V'_{\text{ret}} = V_{\text{ret}} - V_0$ and $t'_{\text{ret}} = t_{\text{ret}} - t_0$ are known as the reduced retention volume and retention time. The reduced parameters do not depend on the fraction occupied by the free volume of the column and on how the latter is packed. In addition to these characteristics, the corrected retention volume is used, equal to the maximum value at $p_1 \rightarrow p_0$: $V_{\text{ret}} = V'_{\text{ret}}f$; the net retention volume $V_{\text{net}} = V'_{\text{ret}}f$, where $f = \frac{3}{2} \frac{(p_1/p_0)^2 - 1}{(p_1/p_0)^3 - 1}$; and also the relative quantities: $V_{\text{rel}} = V_{\text{ret},i}/V_{\text{ret},\text{st}}$ or $t_{\text{rel}} = t_{\text{ret},i}/t_{\text{ret},\text{st}}$ (where p_1 is the pressure at the inlet to the column, and the subscript "ret, st" signifies that the relevant retention volume or time is taken for a standard substance).

When standard substances are used in chromatographic analysis, the interpolation retention characteristics (logarithmic or linear indices) are evaluated. The elution parameters considered above are used for identification of the components in addition to selective columns and detectors, and also to independent identification after separation. The peak areas s or the quantities hl for narrow peaks with a height of h are used for the quantitative interpretation of chromatograms.

The effectiveness of chromatographic separation is determined not only by the processes of dissolving, sorption, and desorption, but also by the nature of the stationary phases, the size of the surface of the solid adsorbent particles, the number of stationary phases, the ratio between the volumes of the solid phase and the free volume, the uniformity of packing, the temperatures, the ways of introducing a sample, and so on. For two components, the separating ability is characterized by the separation factor K_{sep} or the selectivity

coefficient K_s :

$$K_{sep} = \frac{\Delta l}{\sum_i \mu_{0.5, i}} = 0.212 \frac{\Gamma_{0, i} - \Gamma_{0, i+1}}{\Gamma_{0, i}} \sqrt{n};$$

$$K_s = \frac{V_{ret, i+1}^* - V_{ret, i}^*}{V_{ret, i+1}^* + V_{ret, i}^*}$$

where Δl is the difference of the distances between the maxima of the peaks, $\sum \mu_{0.5, i}$ is the sum of their width at half their height, and n is the number of theoretical plates.

For not completely separated peaks, it is more convenient to use the criterion

$$\psi = \frac{h_{sm} - h_{min}}{h_{sm}}$$

where h_{sm} is the height of the smaller peak, and h_{min} is the height of the minimum between the peaks.

Of significance for multicomponent mixtures is the uniformity of separation, a measure of which is the quantity

$$\Delta = \frac{N \tau_{min} K_{eff}}{t}$$

where N is the number of peaks on the chromatogram, τ_{min} is the base of the narrowest peak, t is the duration of analysis, and K_{eff} is the separation factor evaluated according to the individual elution curves for the pair of components separated the least.

The quality of separation is characterized by the peak asymmetry coefficients

$$v_{as} = \frac{\mu_{0.5, r}}{\mu_{0.5, fr}}$$

where $\mu_{0.5, r}$ and $\mu_{0.5, fr}$ are the width of the rear and front of a peak at its half height.

By controlling the indicated effectiveness characteristics, one can choose the optimal conditions of separation.

Experiment 3.1. PHYSICOCHEMICAL CHARACTERISTICS OF ION-EXCHANGE RESINS [2, 4]

The object of the experiment is to see how various factors affect the most important solvation and sorption properties of ion exchangers—their swelling and exchange capacities. The

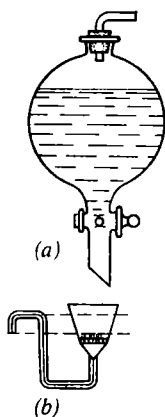


Fig. 3.8. Funnel for washing ion exchangers (a) and funnel with siphon (b)

experiment includes preparation of a commercial sample of an ion exchanger for service (washing off foreign matter, selection of a fraction with the required grain size, transfer into the required ionic form) and experimental determination of the swelling and exchange capacities as functions of the composition of the solution and the conditions of the experiment.

Equipment and Reagents

Equipment and Utensils. An installation for registering activity with a β - and γ -counter. A pH meter. A laboratory shaker. A set of sieves with opening diameters of 0.1, 0.25, 0.5, and 1 mm. A vacuum desiccator. A funnel with a siphon branch tube for washing ion exchangers (Fig. 3.8). Separatory funnels for 1, 0.5 and 0.25 litre. Ordinary funnels (2). A funnel with a glass filter. Burettes for 25 ml (2). Beakers of various volume—from 0.25 to 1 litre (10). A dropping bottle. Measuring flasks for 0.5 litre (2). Flasks for 150 ml with ground-glass stoppers (8). Centrifuge tubes (8). Graduated test tubes for 25-30 ml (8).

Radioactive Substances. A solution containing ^{89}Sr with a known specific activity [$\sim 2 \times 10^6$ cpm/ml].

Reagents. The cation exchanger KU-2 and the anion exchanger AV-17 with a varying content of divinylbenzene (from 2 to 20%). The cation exchangers KU-1 and KB-4. The anion exchangers EDE-10P and AN-22. Ethanol. Acetone. Solutions: 0.5 *N*, 1 *N*, 3*N*, and 6 *N* HCl; 0.25 *N*, 1.2 *N*, and 2*N* NaOH; 1 *M*, 2 *M*, and saturated NaCl; 1 *M* and 2 *M* SrCl_2 ; 0.2 *M* YCl_3 ; 0.2 *M* ThCl_4 ; 0.05 *M* AgNO_3 ; 0.5 *M* NH_4CNS ; 0.3 *M* Na_2SO_4 ; 0.25 *M* NH_4OH .

Performance of Work

(a) Preparation of Ion Exchanger for Work

Keep a weighed portion of a commercial ion exchanger (~200 g) for 6-12 hours in a saturated solution of sodium chloride with periodic shaking. Next transfer the ion exchanger into a large separatory funnel in which its further treatment is performed.

First treat a cation exchanger with a solution of sodium hydroxide (about 15 volumes of a 5% solution per volume of ion exchanger) until the colour in the filtrate vanishes. Next, after washing with water, perform acid treatment, first using a 1 *N* solution of HCl (about 5 volumes per volume of ion exchanger), then a 3 *N*, and, finally, a 6 *N* solution of HCl up to complete vanishing of iron in the filtrate (test with ammonium thiocyanate). If the iron is washed off too slowly, the resin may be treated with a solution of ammonium thiocyanate with the following washing with water, hydrochloric acid, and again water. After the acid treatment, condition the cation exchanger by alternately treating it with a 1-2 *N* solution of alkali, water, a 1-2 *N* solution of acid, water, and so on, repeating the alkali-acid cycle at least three times. The volumes of the alkali and acid in conditioning must exceed that of the ion exchanger two or three times. It must be noted that for obtaining reproducible results when working with ion exchangers, the conditioning operation must be repeated every 4-6 months. After the final acid treatment of the cation exchanger, wash it with distilled water to remove the chloride ion (test with silver nitrate).

First wash an anion exchanger repeatedly with 0.5 *N* hydrochloric acid until the colour of the filtrate vanishes. Next, after washing it with water, treat it with an alkali solution of gradually growing concentration (from 1 to 4 *M*). After this, condition the anion exchanger by alternately treating it with an acid and an alkali, wash off the chloride ion, and then wash it with water up to a weakly alkaline reaction of the washing water.

For additional purification from organic contaminants, it is good practice to treat them with several volumes of 95% ethanol, and then again wash them with water.

To transfer an ion-exchange resin to the salt form needed for work, treat an H-cation exchanger or an OH-anion exchanger prepared as described above in a funnel for washing (Fig. 3.8) with a 2 *M* solution of the relevant salt (about 15 volumes of the solution per volume of ion exchanger), and then thoroughly wash off the excess electrolyte with distilled water.

Dry the treated ion exchangers. A strongly acidic cation exchanger may be dried in air or with slight heating (60-80 °C) up to a constant mass. It is not recommended to heat an anion exchanger to above 40 °C.

A cation exchanger may be stored either in the dry form or in a swollen state. Strongly basic anion exchangers (of type AV-17) in the OH form are to be stored only under water.

Pass the prepared and dried ion exchanger through the set of sieves and choose the fraction needed for work (usually with a particle diameter of 0.25-0.5 mm). When it is necessary to work with ion exchanger fractions of a small grain size, use the differences in the rate of settling of a suspension of the ion exchanger in water to separate the fractions by grain size.

(b) Determining the Degree of Swelling of an Ion Exchanger

Place a weighed portion (1.0-1.5 g) of dehydrated (for example, over P_2O_5) ion exchanger brought up to a constant mass at 105 °C into a graduated test tube for 25-30 ml with a ground-glass stopper. Compact the resin, and note the volume it occupies. Next cover the resin with 20 ml of a solution of the required composition and shake it in the shaker during one hour. Centrifuge the solution and measure the volume of the swollen resin.

Calculate the relative degree of swelling *A* of the ion exchanger (in %) by the formula

$$A = \frac{V_1}{V_2} 100$$

where V_1 and V_2 are the volumes of the swollen and dry ion exchanger, respectively.

Perform three parallel measurements for each composition of the solution.

See how the following factors affect the degree of swelling of an ion exchanger:

1. The nature of the exchanger. Use cation exchangers of the following grades: strongly acidic KU-2, strongly acidic macroporous KU-23, weakly acidic KB-4; polyfunctional KU-1, and anion exchangers of the grades: strongly basic AV-17 and AV-17P, moderately basic EDE-10P, and weakly basic AN-22.

2. The degree of cross-linking of the ion exchanger. Use a cation exchanger KU-2 or Dowex-50 with a content of divinylbenzene of 2, 4, 8, 12 and 24%.

3. The charge and the nature of the counterion. Use the cation exchanger KU-2 in the forms RH, RNa, R_2Sr , R_2Ca , R_3Y , R_4Th , or the anion exchanger AV-17 in the forms ROH, RCl, and R_2SO_4 in an aqueous solution.

4. The nature and concentration of the solvent. Use the cation exchanger KU-2 in the H and Na form in an aqueous solution and with a content of 20, 40, 60, 80 and 90% of ethanol or acetone, or the anion exchanger AV-17 in the Cl- and OH-forms in the same solvents.

5. The concentration of the external solution. Use the cation exchanger KU-2 in the Ca form and aqueous solutions of $CaCl_2$ with a concentration from 0.05 M to saturation.

Use the results obtained to see how the factors studied affect the swelling capacity of ion-exchange resins.

(c) Determination of Exchange Capacity of Ion Exchangers

Determination of Capacity by Replacing Counterion

Monofunctional Strongly Acidic Cation Exchangers and Strongly Basic Anion Exchangers. Soak a weighed portion (~2 g) of dry-weight cation exchanger KU-2 in the H form several hours in a 2 N hydrochloric acid (a weighed portion of an anion exchanger in 2 N solution of sodium hydroxide). Place the moist ion exchanger in a funnel with a siphon (see Fig. 3.8); if it is a cation exchanger, treat it from a dropping funnel with a solution of HCl, and if it is an anion exchanger, with a solution of NaOH. Next wash the exchanger to remove the sodium or chloride ions, respectively (the duration of the above procedures is 4-5 h). Shake the ion exchanger pre-

pared in this way (H-cation exchanger or OH-anion exchanger) in a separatory funnel with periodically renewed portions of an NaCl solution (each portion is 50 ml of a 2 *M* solution) until the filtrate becomes almost neutral ($6 < \text{pH} < 8$). Titrate an aliquot sample of the combined filtrate in the presence of phenolphthalein with a solution of NaOH or HCl, respectively (run two parallel experiments).

Use the data obtained to calculate the exchange capacity of the cation exchanger relative to hydrogen (of the anion exchanger relative to the hydroxyl groups) in milliequivalents per gramme of dry-weight ion exchanger.

Polyfunctional (KU-1) and Weakly Acidic (KB-4) Cation Exchangers. Pour 100 ml of a 2 *N* solution of NaOH in a 1 *M* solution of NaCl over a weighed portion of freshly prepared cation exchanger (~ 1 g) in the H-form placed in a flask and let it stand overnight. Separate the solution from the ion exchanger and titrate an aliquot part of the filtrate (10 ml) with 0.05 *N* HCl in the presence of phenolphthalein. Calculate the total exchange capacity of the ion exchanger (in mequiv/g).

Wash another weighed portion (~ 2 g) of the cation exchanger in the H-form on a glass filter with 200 ml of a 0.3 *M* neutral solution of Na_2SO_4 supplied from a separatory funnel. Collect the filtrate in a measuring flask and titrate an aliquot part (10 ml) with a 0.05 *M* solution of AgNO_3 in the presence of phenolphthalein. Calculate the capacity of the ion exchanger according to the strongly acidic groups.

Polyfunctional Anion Exchanger (EDE-10P). To determine the capacity with respect to strongly basic groups, treat a weighed portion (1 g) of an anion exchanger in the Cl-form on a filter with 200 ml of a 0.25 *M* solution of ammonia added from a dropping funnel. Collect the filtrate in a measuring flask. Determine the concentration of the evolved chloride ion by titrating an aliquot part of the solution with a 0.05 *M* solution of AgNO_3 .

To determine the capacity with respect to weakly basic groups, wash a weighed portion (1 g) of an anion exchanger with 200 ml of a 0.3 *M* solution of Na_2SO_4 . Determine the content of chloride ions in the filtrate by titration with a 0.05 *M* solution of AgNO_3 .

By summation of the capacity values found in the first and second cases, find the value of the total exchange capacity of the polyfunctional anion exchanger.

Determination of the Exchange Capacity of Ion Exchangers by Potentiometric Titration

Put 1.00 g of the cation exchanger KU-2 in the H-form into each of seven 150-ml flasks with ground-glass stoppers and add 100 ml of an NaOH solution of various concentrations. The solutions can be prepared by mixing water and a 0.25 *N* solution of NaOH in the following proportions:

Flask No.	1	2	3	4	5	6	7
Volume of water, ml	100	90	75	50	30	20	10
Volume of 0.25 <i>N</i> solution of NaOH, ml	0	10	25	50	70	80	90

Close the flasks with the resin and solution with their stoppers and place them for 10-12 h into the laboratory shaker. Next pour the solutions off the ion exchanger and measure the pH of the filtrates with the aid of a lamp pH meter with a glass electrode.

Plot the values of the pH of an equilibrium solution against the amount of added NaOH (in mequiv). Determine the value of the total exchange capacity according to the position of the point of inflection.

Run the experiments with the polyfunctional cation exchanger KU-1 and the weakly acidic exchanger KB-4 in a similar way, determining how the exchange capacity of these exchangers depends on the pH of the solution. Increase the time needed for equilibrium to set in up to seven days.

Using water-acid mixtures of various compositions instead of the water-alkaline ones, determine the total exchange capacity of the anion exchanger AV-17, and also the dependence of the capacity on the pH for the anion exchangers EDE-10P and AN-22.

Determination of the Exchange Capacity of Ion Exchangers by the Method of Isotope Dilution

If an ion exchanger is first saturated with ions of an element in a solution of a definite concentration, and is then brought into contact with the solution of the same concentration, but containing a radioactive isotope of this element, then after equilibrium has set in the specific activity of the isotope in the phase of the ion exchanger and the solution

should be the same. Having measured the initial and equilibrium activity of the solution, we can evaluate the total exchange capacity Q of the ion exchanger by the formula

$$Q = \frac{Vc}{m} \left(\frac{I_0}{I} - 1 \right) \quad (3.12)$$

where V is the volume of the solution, ml, c is the concentration of the counterion in the solution, mequiv/ml, m is the mass of the cation exchanger, g, and I_0 and I are the initial and equilibrium activities of the solution, cpm.

Transfer the cation exchanger KU-2 into the Sr form. For this purpose, keep a weighed portion (~ 20 g) of the cation exchanger in a 1 M solution of SrCl_2 until equilibrium sets in. Filter off the solution, and wash the cation exchanger several times with water, and then dry it up to a constant mass at 105°C . Put 2 g of the cation exchanger into each of 6 centrifuge tubes and pour in 20 ml of a 1 M solution of SrCl_2 containing ^{89}Sr with a specific activity of ~ 2000 cpm/ml. Pour a radioactive solution of the same composition into a seventh tube, but add no ion exchanger. Place the tubes into the shaker. Remove the tubes one by one after 30 min, 1, 2, 3, 4, and 6 h of stirring, decant or filter off the solution, and measure the activity of its aliquot part. Determine the specific activity of the initial solution by measuring the activity of the solution in the seventh tube. Use the experimental data to plot the activity of the solution against the duration of its contact with the ion exchanger. Find the time corresponding to equilibrium activity from the plot. Use formula (3.12) to evaluate the total exchange capacity of the ion exchanger and compare it with the values found for the given batch of ion exchanger by other methods.

Experiment 3.2. STUDYING THE SELECTIVITY OF ION EXCHANGE [2, 3, 4]

The object of this experiment is to study how various factors affect the values of the distribution coefficients of different elements in ion exchange.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β - and γ -radiation. A thermostatted shaker. Round-bottom conical flasks for 30 ml with ground-glass stoppers (8). Graduated test tubes (8). Beakers for 200 ml (2). A medical syringe. Pipettes for 1 and 10 ml. Measuring bowls.

Radioactive Substances. Solutions containing ^{86}Rb , ^{45}Ca , ^{140}Ba , ^{91}Y , or ^{143}Pr without a carrier (the specific activity of each solution is about 2.0×10^5 cpm/ml).

Reagents. Cation exchanger KU-2 in the H, Na, and Ca forms. Solutions: 0.05, 0.1, 1.0, and 2.0 M SrCl_2 ; 0.1 M NaCl ; 0.05 and 0.1 M CaCl_2 ; 0.1 M RbCl ; 0.1 M BaCl_2 ; 0.1 M YCl_3 .

Performance of Work

Procedure for Determining the Distribution Coefficients

Put weighed portions of the cation exchanger in the H or salt form and definite volumes of a solution containing the element being studied labelled with its radioactive isotope into 30-ml flasks with ground-glass stoppers. Stir the phases in the thermostatted shaker at a temperature of $25 \pm 1^\circ\text{C}$ during the time needed for achieving equilibrium (for aqueous solutions, the duration of shaking is 3-3.5 h). Upon the completion of shaking, separate the solution from the ion exchanger (by filtration or better by decanting) and measure the activity of the aliquot part of the solution placed in the measuring bowls (after evaporation or without it). Use the difference between the activity values for the initial and equilibrium solutions to calculate the amount of substance absorbed by the weighed portion of the ion exchanger, and calculate the distribution coefficient by formula (3.7) according to the obtained data.

Influence of Concentration of Ions Being Exchanged on K_d . Perform the investigation according to the procedure described above for a constant V/m ratio (for example, $V/m = 200$; 0.1 g of ion exchanger + 20 ml of solution). Use the cation exchanger KU-2 in the Na-form and solutions of SrCl_2 with a concentration of 10^{-6} , 10^{-5} , 10^{-4} , 10^{-3} , and 10^{-2} M at a constant ionic strength of the solutions (0.1) achieved by adding calculated amounts of a 0.1 M solution of NaCl to each solution. Add 1 ml of the solution containing ^{89}Sr to each flask. Distribute each composition

of the solution among three-flasks—shake two of them with a weighed portion of the ion exchanger and the third one without it. Determine the specific activity of each solution using this third solution.

In a similar way, determine how the distribution coefficient for $^{45}\text{CaCl}_2$ depends on the carrier concentration. Evaluate the separation coefficients of calcium and strontium.

Dependence of K_d on the V/m Ratio. Perform the experiments according to the procedure described above. Use the cation exchanger KU-2 in the Na form. Keep the carrier concentration constant (for example, 0.05 M or without a carrier). Vary the ratio V/m , for example, as follows.

Experiment No.	I	II	III	IV	V	VI
m of cation exchanger, g . . .	0.25	0.5	0.75	1	2	0.25
V of solution, ml	15	15	15	15	15	30

Repeat each experiment twice. Evaluate the distribution coefficients and appraise their dependence on the V/m ratio.

Influence of Ion Charge. Perform the experiments according to the procedure described above. Use the cation exchanger KU-2 in the Na and Ca forms and solutions, for example, of the chlorides $^{86}\text{RbCl}$, $^{89}\text{SrCl}_2$, and $^{91}\text{YCl}_3$ of equimolar concentrations. On the basis of experimental results, calculate the distribution coefficients and see how the ion charge affects the selectivity of ion exchange.

Influence of Counterion Radius. Perform the experiments according to the procedure described above. Use the cation exchanger KU-2 in the Na and Ca forms and solutions of $^{45}\text{CaCl}_2$, $^{89}\text{SrCl}_2$, and $^{140}\text{BaCl}_2$ of equimolar concentrations. Calculate the distribution coefficients on the basis of the experimental data and see how the radius of a counterion affects K_d .

Determination of Separation Coefficient of Ions by Static Method

Place 0.25 g of the resin KU-2 in the Na form into each of four test tubes. Pour 15 ml of a mixture of equimolar amounts of SrCl_2 and CaCl_2 labelled with the corresponding isotopes (for example, 0.05 M solutions of $^{89}\text{SrCl}_2$ and

$^{45}\text{CaCl}_2$ with a specific activity of about 10^4 cpm/ml) into the first tube and shake it in the shaker for 1-1.5 h. After this, transfer two 0.5-ml samples from the solution into bowls for measuring activity, pour the remaining solution into the second tube, and shake it for another 1-1.5 h. Again take two samples, pour the remaining solution into the next test tube, and so on. Dry the solutions in the bowls, and measure the activity of the dry residue two times in an instrument with an end-window counter—without a filter and with an aluminium filter whose thickness is sufficient for complete absorption of the β -radiation of ^{45}Ca . Use the results of the measurements with account taken of the filter thickness to calculate the activity of the ^{89}Sr in the sample taken. Subtracting the found value from the activity of the sample measured without a filter, determine the activity of the ^{45}Ca in the sample.

Use the ratios of the activities of ^{45}Ca and ^{89}Sr in each test tube to calculate the distribution and separation coefficients of the selected ions on the ion exchanger (take into consideration the change in the volumes of the solutions because of taking the samples). Compare the found values of K_d and K_{sep} with those calculated according to the data of the experiment devoted to studying the influence of the concentration of ions on K_d .

Experiment 3.3. ION-EXCHANGE CHROMATOGRAPHIC SEPARATION OF RADIOACTIVE ISOTOPES [4, 9-13]

The experiment is divided into a number of variants illustrating the various principles underlying ion-exchange separations.

Equipment and Reagents

Equipment and Utensils. An arrangement for the automatic registration of the activity of a filtrate (Fig. 3.9). An instrument for registering activity with an end-window or β -, γ -counter. A pH meter. A photoelectric colorimeter. Chromatographic columns: ordinary and with a side offtake. Microcolumns. A medical syringe. Beakers for 50 and 100 ml. Pipettes for 0.2, 1, and 5 ml. A wash bottle. A dropping bottle. Burettes. Bowls for measuring the activity.

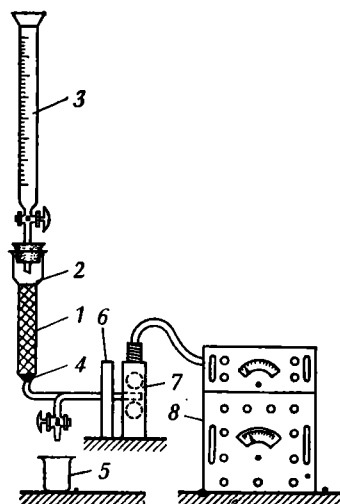


Fig. 3.9. Arrangement for automatic registration of a filtrate activity:

1—chromatographic column with ion exchanger; 2—upper level of resin in column; 3—burette for supplying washing solution; 4—glass wool seal (or glass filter) at column outlet; 5—receiver of eluate; 6—lead shielding wall; 7—radiometer transmitter; 8—radiometer

Radioactive Substances. Solutions containing radioactive isotopes with a specific activity of about 10^6 cpm/ml:

Variant of

experiment	a	b	c
Isotopes .	$^{59}\text{Fe} + ^{60}\text{Co}$	$^{86}\text{Rb} + ^{137}\text{Cr}$	$\text{UO}_2(\text{NO}_3)_2$ (200 mg of U in 50 ml)

Variant of

experiment	d	e	f
Isotopes .	$^{59}\text{Fe} + ^{51}\text{Cr}$	$^{140}\text{Ba} + ^{140}\text{La}$	$^{90}\text{Sr} + ^{90}\text{Y}$

Variant of

experiment	g	h	i
Isotopes .	$^{48}\text{Ca} + ^{89}\text{Sr} + ^{133}\text{Ba}$	$^{152}\text{Eu} + ^{143}\text{Pr} + ^{141}\text{Ce}$	$^{152}\text{Eu} + ^{141}\text{Ce}$

Reagents. a. Cation exchanger Dowex-50 X4 with a grain size of 50-100 mesh (approximately 0.1-0.25 mm) or KU-2 X6 in the H form; 0.2 N, 0.8 N, and 4 M HCl.

b. Cation exchanger KU-1 in the H form; 5.5 M HCl.

c. Cation exchanger KU-2X6 (or X8) in the H form. Solutions: 0.5 N HCl; 5% $\text{H}_2\text{C}_2\text{O}_4$; 1% $\text{K}_4[\text{Fe}(\text{CN})_6]$; 0.1% arsenazo I.

d. Cation exchanger Dowex-50 X4 with a grain size of 50-100 mesh or KU-2X6 in the Na form. Solutions: 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ acidified with HCl to a pH of 2; 2 N H_2SO_4 .

e. Cation exchanger KU-2X6 (or X8) in the H form. Solutions of 5% citric acid; 6 M and 0.6 M ammonia.

f. Anion exchanger EDE-10P (citrate form); solutions: 1 N HCl, 5% citric acid, 6 M and 0.6 M ammonia.

g. Cation exchanger Dowex-50 X12 with grain size of 100-200 mesh in the NH_4 form. Solutions: 2 M and 4 M $\text{NH}_4\text{CH}_3\text{CO}_2$.

h. Cation exchanger Dowex-50 X12 with grain size of 200-400 mesh in the NH_4 form. Solutions: 3.6% lactic acid (preliminarily purified of oxidation and dimerization products by distillation in a vacuum); 6 M and 3 M ammonia.

i. Cation exchanger Dowex-50 X4 in the Na form; 0.12 M solution of mandelic acid (0.06 M with respect to NaOH) in 40% acetone.

Performance of Work

Separate the isotopes by means of the elution method using the general procedure described herein. The compositions of the eluting solutions and additional information relating to the conditions of separation are indicated more specifically under the relevant headings (a-i).

Soak the ion exchanger preliminarily transferred to the required ionic form (see Experiment 3.1) for 4-6 h in water, load it into a chromatographic column and wash it with 4-5 volumes of the solution (per volume of the column) of the same composition as the solution from which sorption is to be performed, or as the first eluting solution (this solution naturally contains no radioactive isotope). Drain off the surplus of the washing solution almost to the upper layer of the ion exchanger (the resin should remain only slightly moistened) and at this instant introduce (for example, with the aid of a pipette with a drawn out tip) into the upper part of the column the solution being analysed containing a mixture of the isotopes to be separated in a minimum volume (1-3 drops). The initial activity of the solution should exceed the background of the registering instrument by 2-3 orders. After the radioactive solution is absorbed into the resin, introduce the first eluting solution into the top part of the column, seeing that no swelling of the ion exchanger occurs. Establish and maintain a constant (for example, with the aid of a Boyle seal) rate of elution—usually within the interval from 0.5 to 1 ml/min (when using standard laboratory columns). Collect the eluate in portions of a definite volume (for example, with the aid

of an automatic sampler-collector) and determine the content of the relevant isotope in an aliquot part of each fraction by radiometric means. When separating isotopes with a sufficiently hard β - or γ -radiation, one can use an arrangement with continuous automatic registration of the filtrate activity at the outlet from the column. Such an arrangement is shown schematically in Fig. 3.9.

Use the results of separation to plot an elution curve in the coordinates: volume of solution passed through the column versus filtrate activity. Determine the free volume of the column (for example, by passing through it a solution containing a radioactive isotope not absorbed by the given ion exchanger and measuring the volume of the filtrate from the instant of introducing the indicator to the appearance of activity in the filtrate). Calculate the separation coefficient for the studied ions as the ratio of the distances of the elution peaks from the point on the axis of abscissas corresponding to V_{tr} .

It may be necessary to determine the quantitative composition of the mixture being chromatographed. For this purpose, calculate the magnitude and ratio of the areas under the elution peaks of the corresponding ions on the chromatogram. It is necessary to first graduate the installation using solutions of the isotopes in the mixture with a known activity.

Check the radiochemical purity of the isotopes in the separated fractions, determining either the radiation energy with the aid of an analyser or the half-life, if possible.

a. Separation of ^{59}Fe and ^{60}Co

This experiment is an example of the displacement elution of ions sorbed on a cation exchanger by hydrogen ions. First the ion having a lower value of the exchange constant, i.e. Co^{2+} , is eluted with dilute hydrochloric acid, and then the ion Fe^{3+} . For washing out of the second component to occur more rapidly and with less blurring, increase the concentration of the hydrochloric acid after washing out of the cobalt.

Wash the column with the cation exchanger with 0.2 *N* HCl and introduce the mixture of ions being separated in the minimum volume of a weakly acidic solution. Elute the ^{60}Co with 0.8 *N* HCl, after which wash out the ^{59}Fe with 4 *M* HCl.

b. Separation of ^{86}Rb and ^{137}Cs

When separating these isotopes, use the ability of the phenol groups of the ion exchanger KU-1 of selectively complexing with the heavier of the alkali metal ions.

Sorb the ions being analysed in the column with the cation exchanger KU-1 from 0.1 *N* HCl. Elute both isotopes with separation using 5.5 *M* HCl.

c. Separation of U and UX_1

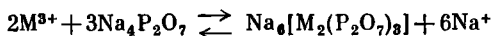
The thorium isotope ^{234}Th (UX_1) is a convenient ($T_{1/2} = 24$ days) β^- -radioactive indicator of thorium.

The separation is based on the inability of thorium (unlike many other metals, including uranium) to form complexes with the Cl^- ion.

Pass a solution of uranyl nitrate (200 mg of U in equilibrium with UX_1 in an aqueous solution) through a column with a cation exchanger. Next completely wash out the uranium with 0.5 *N* HCl. Control the end of washing out by means of a drop reaction with $\text{K}_4[\text{Fe}(\text{CN})_6]$. After washing the ion exchanger with water, elute the UX_1 with 50 ml of 5% oxalic acid. Determine the amount of UX_1 in the filtrate samples after evaporation according to the β^- -radiation of the equilibrium UX_2 . Determine the presence of uranium in the eluate by colorimetric means, for example by using arsenazo I (see Experiment 11.2 E in Vol. 2).

d. Separation of ^{59}Fe and ^{51}Cr

The separation of these isotopes is based on the different strength in acid solutions of the pyrophosphate complexes of Fe^{3+} and Cr^{3+} formed according to the reaction



At pH = 2, the chromium complex is not stable.

After absorption of the components of the mixture being separated by the cation exchanger, use a 0.1 *M* solution of sodium pyrophosphate acidified with hydrochloric acid to pH = 2 (use thymol blue as an indicator) for elution of the ^{59}Fe . After elution of the iron (control according to the filtrate activity), wash the ion exchanger with water, and then desorb the ^{51}Cr with 2 *N* H_2SO_4 .

e. Separation of ^{140}Ba and ^{140}La

The separation is based on the difference in the strength of citrate complexes of lanthanum and barium.

Sorb the isotope ^{140}Ba (in equilibrium with ^{140}La) from a 0.1 *N* HCl solution on the cation exchanger, and then wash the resin with water. Wash out the ^{140}La with 5% citric acid neutralized with ammonia to pH = 3.0. Next elute the ^{140}Ba with 5% citric acid at pH = 5.0. Control the purity of the separated ^{140}La by measuring in definite time intervals (1-3 h) the activity of preparations obtained from eluate fractions corresponding to the first peak. Use the curve $\log I$ versus t to determine the half-life of ^{140}La .

f. Separation of ^{90}Sr and ^{90}Y

Sorb the isotope ^{90}Sr (in equilibrium with ^{90}Y) on an anion exchanger. Wash out the ^{90}Sr with citric acid neutralized with ammonia to a pH of 3.5, after which elute the ^{90}Y with 1 *N* HCl.

g. Separation of ^{45}Ca , ^{89}Sr , and ^{133}Ba

Sorb the mixture of the three ions in a column with a cation exchanger from a weakly acidic (almost neutral) solution. Use solutions of ammonium acetate as the eluents. Elute the ^{45}Ca and ^{89}Sr (with separation) with a 2 *M* solution of $\text{NH}_4\text{CH}_3\text{CO}_2$, and the ^{133}Ba with a 4 *M* one.

h. Separation of Radioactive Isotopes of Rare-Earth Elements (^{152}Eu - ^{143}Pr - $^{141}\text{Ce}^*$)

In the complex-formation chromatography of rare-earth elements, solutions of lactic and α -hydroxy isobutyric acids are the most frequently used eluents.

Place the swollen cation exchanger into a microcolumn with dimensions of 175×2 mm connected to a device for supplying the eluent under pressure. Use a 3.6% solution of lactic acid neutralized with ammonia to a pH of 3.5 as the

* Mixtures of other isotopes of the rare-earth elements may be used.

eluent. Sorb the mixture of rare-earth isotopes from one drop of a weakly acidic solution. Maintain a constant rate of filtration (about 1 drop/min). Collect the filtrate in portions of 1-2 drops, and after drying, measure the activity of the samples. The filtrate can be collected by drops on a moving ribbon of filter paper passed under the window of an end-window counter. The duration of separating the mixture of three isotopes in the given case is seven or eight hours.

*i. Separation of ^{152}Eu and ^{141}Ce
with Aqueous-Acetone Solutions
of Mandelic Acid*

In the given experiment, an increase in the effectiveness of cation-exchange separation of elements close in their properties is achieved by combining two factors: the use of a complexing agent— α -hydroxy acid and the replacement of the aqueous medium with a mixed aqueous and organic solvent.

Sorb the isotopes in the upper part of the column with a cation exchanger in 1-2 drops of a weakly acidic solution. Use a 0.12 *M* solution of mandelic acid (0.06 *M* with respect to NaOH) containing 40% of acetone by volume as the eluent.

Calculate the separation coefficients of the selected pair of isotopes and compare them with the separation coefficients obtained when using lactate solutions as eluents (see Sec. h).

**Experiment 3.4. SEPARATION OF RADIOACTIVE
ISOTOPES BY PAPER CHROMATOGRAPHY [6, 14]**

In the present experiment, it is proposed to appraise the effectiveness of separating pairs of isotopes such that often accompany each other and lend themselves to separation with difficulty. Particularly, in practice we have to do with mixtures of zinc and cadmium or iron and chromium either in commensurable amounts or with a large surplus of one of the elements.

A. SEPARATION OF ^{65}Zn AND ^{115}Cd

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter (or an installation for the automatic registration of paper strips). A chromatographic chamber (Fig. 3.10). Chromato-

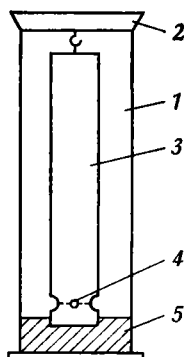


Fig. 3.10. Chamber for paper chromatography:
 1—glass cylinder; 2—lid; 3—paper strip; 4—place where mixture of substances being separated is applied; 5—solvent

graphic paper No. 2 of Grade "B" (fast). An infrared lamp. A straight-edge (25 cm). A micropipette for 0.1 ml. A beaker for 200 ml.

Radioactive Substances. A 10^{-4} M solution of ZnCl_2 containing ^{65}Zn with a specific activity of $\approx 80\,000$ cpm/ml; a 10^{-4} M solution of CdCl_2 containing ^{115}Cd with a specific activity of $\approx 80\,000$ cpm/ml.

Reagents. Solvent I consisting of a mixture of methanol, 25% ammonia, and water in the proportion 11 : 6 : 3 (by volume).

Performance of Work

Use the method of ascending paper radiochromatography with solvent I for separating a mixture of zinc and cadmium chlorides at a concentration thereof of the order of 10^{-4} M.

First saturate the chromatographic chamber with the vapour of the solvent. For this purpose, pour solvent I onto the bottom of the chamber, close the latter, and let it stand for an hour to saturate its space with the vapour. Cut out three strips $3 \times 16\text{ cm}^2$ in size from chromatographic paper. Shape the lower part of a strip as shown in Fig. 3.10. Mark the starting line with a pencil 2 cm above the bottom edge of the strip, and the finish line 8 cm above the starting one. Draw a circle 6 mm in diameter at the middle of the narrow part with a pencil and mark the starting line. Apply to the drawn spot 0.1 ml of the solution of isotope dropwise with the micropipette: onto the first paper strip— ^{115}Cd , onto the second one— ^{65}Zn , and onto the third one a mixture of these isotopes with an activity of $\approx 40\,000$ cpm. Carefully

dry the paper strips under the infrared lamp, then hang them so that half of the bottom part of a strip is immersed into the solvent, and let them stand until the front of the solvent reaches the finish line. Upon completion of development of the chromatogram, carefully extract it from the chamber and dry it in a stream of warm air.

Use the registering device to measure the activity in the direction of travel of the solvent front. For measurements in the end-window counter, cut up the chromatogram into separate strips 5 mm long, number them in sequential order, and measure the activity of each portion in the counter, placing the preparation in a wax paper envelope on a special holder*. It is even better, if allowed by the instrument, to move the strip without cutting it under the window of the end-window counter and measure the activity of each section along the entire strip.

Plot the activity against the distance of a section from the starting line. Determine the distance from the starting line to the section with the maximum activity.

Find the value of R_f for each isotope. Calculate the isotope separation coefficient. Determine the absolute values of the activity of each isotope and find their content in the mixture being studied.

B. SEPARATION OF ^{59}Fe AND ^{51}Cr

Equipment and Reagents

Equipment and Utensils. The same as in Sec. A of the given experiment.

Radioactive Substances. A 10^{-4} M solution of FeCl_3 containing ^{59}Fe with a specific activity of $\approx 80\,000$ cpm/ml. A 10^{-4} M solution of CrCl_3 containing ^{51}Cr with a specific activity of $\approx 80\,000$ cpm/ml.

Reagents. Solvent II consisting of a mixture of acetone and 6 M hydrochloric acid taken in a proportion of 9 : 1 (by volume).

Performance of Work

Use solvent II for separating iron and chromium by the method of paper chromatography.

Prepare for work and saturate the chromatographic chamber with the solvent vapour as described in Sec. A of this

* It is recommended to mark the cutting lines and number the strip sections preliminarily, before chromatographing.

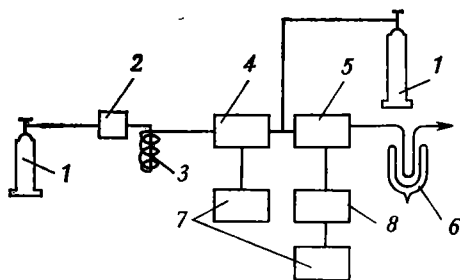


Fig. 3.11.

Gas-liquid chromatograph:

1—cylinders with helium and methane; 2—vaporizer; 3—chromatographic column; 4—katharometer; 5—cylindrical flow-type counter; 6—trap for freezing out vapour; 7—recording potentiometers; 8—device measuring the counting rate

experiment. Apply 0.1 ml of active solutions of FeCl_3 , CrCl_3 , and their mixture at the starting line on each of three paper strips. Next proceed as described in Sec. A.

After measuring the activity of the strips, plot the activity against the distance and determine the distance corresponding to the maximum value of the activity. Find the value of R_f for each isotope. Calculate the separation coefficient. Appraise the ratio of the isotopes (according to their activity) in the studied mixture.

Experiment 3.5. SEPARATION AND ANALYSIS OF MIXTURES OF ORGANIC COMPOUNDS LABELLED WITH ^{14}C AND ^3H BY GAS-LIQUID CHROMATOGRAPHY [7, 8]

The object of the experiment is to separate a mixture of labelled substances by gas-liquid chromatography, to identify the mixture components according to their elution characteristics, and also to determine the content of the components and appraise the effectiveness of separation.

The experiment is performed in a gas-liquid chromatograph with detection according to the radioactivity and to the thermal conductivity (Fig. 3.11). A chromatographic column 2 m long and 3-5 mm in diameter, placed in a thermostat, is filled with diatomite (the fraction with a grain diameter of 0.25-0.5 mm) with the liquid phase applied (β, β' -hydroxydipropionitrile). The liquid phase is 10%

of the mass of the solid carrier. The column inlet is joined to systems of purification, control, and measuring of the rate of flow of the carrier gas with a vaporizer for introducing the samples to be studied. At the column outlet, there are consecutively arranged thermostatted detectors: a katharometer and a flow-type proportional counter, and also a trap for freezing out the vapours of the separated labelled substances and a foam-type rate-of-flow meter. The proportional counter is the transmitter of the device for measuring the radioactivity of the labelled components of the mixture separated by the chromatographic column.

Equipment and Reagents

Equipment. A device for measuring activity with a cylindrical flow-type counter. A gas-liquid chromatograph with double detection according to the thermal conductivity and the radioactivity. A cylinder with the carrier gas. A foam-type gas rate-of-flow meter. A microsyringe for 0.1 ml with a micrometric screw.

Radioactive Substances. Sealed ampoules with a mixture of organic substances labelled with ^{14}C or ^3H (including one with an equimolar mixture of cyclohexane, benzene, and toluene) having a specific activity of 3.7 MBq (1 μCi). A sealed ampoule with labelled benzene having a specific activity of 3.7 MBq (1 μCi). A preparation of radioactive ^{137}Cs (standard) with an activity of 50 000-100 000 cpm.

Performance of Work

Before commencing work, acquaint yourself with the design of the chromatograph and the procedure for working with the systems of registering the signal of the katharometer and the proportional counter. Admit a stream of the carrier gas and lighting gas (from the main) into the chromatograph. Switch on the heaters of the thermostats, setting a temperature of 67 °C for the column and of 100 °C for the detectors. Switch on the detection systems. When the temperatures of the thermostats reach their preset values, use the foam-type gas rate-of-flow meter to set a carrier gas rate of flow of 20 ml/min, and a lighting gas rate of flow of 40 ml/min. Set the operating conditions for the katharometer and the proportional counter. Obtain a counter plateau using a standard preparation of ^{137}Cs . Determine the background of the counter.

Switch on the heaters and bring the temperature in the vaporizer up to 120 °C. Open the cooled ampoule with la-

belled benzene and take a 0.015-ml sample with the microsyringe. Introduce the sample into the vaporizer and mark the time of introducing the sample on the tape of the recording instruments. After passing of the benzene peak, open the cooled ampoule with the mixture of labelled substances. Take a 0.015-ml sample with the cleaned syringe and introduce it into the heated vaporizer, marking the time of introducing the mixture on the tape of the recording instrument. Switch off the vaporizer heaters.

In an hour after introducing the sample, switch off the detection systems and the heaters of the thermostats. Stop the supply of gases into the installation.

Determine the retention distance and evaluate the retention time for each peak on the chromatograms. Taking the retention time of benzene as unity, calculate the relative retention time for each component; using the data given in Table 3.1, identify the peaks. Calculate the degree of separation and the selectivity coefficients.

Table 3.1. Relative Retention Volumes of Hydrocarbons

Hydrocarbon	Relative retention volume		Hydrocarbon	Relative retention volume	
	25 °C	67 °C		25 °C	67 °C
<i>n</i> -Pentane	1.00	1.00	Cyclohexene	18.3	11.2
Cyclopentane	3.4	2.9	Benzene	—	45
Cyclopentene	6.4	4.6	Toluene	—	81
Cyclohexane	6.8	5.0	Ethylbenzene	—	130

The area of the benzene peaks registered in analysing pure benzene and its mixture with other substances is used to assay the benzene content in the mixture.

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Chapter 4 Electrochemistry of Radioactive Isotopes

THEORETICAL INTRODUCTION [1]

Electrochemistry of radioactive isotopes and elements is widely used when studying the chemical and physicochemical properties of radioactive elements, the state of radioactive isotopes in solutions, when separating radioactive isotopes in a chemically and radiochemically pure state, and also when preparing sources of radioactive radiations.

When studying electrochemical processes in solutions of radioactive isotopes, two cases are encountered: (1) the radioactive isotope is in the solution in a low (10^{-6} - 10^{-3} mol/litre) concentration, and (2) in an ultradilute state (the concentration of the isotope is below 10^{-6} - 10^{-7} mol/litre).

In the first case, the features of behaviour of radioactive isotopes are associated with the radiation action of their

intrinsic radiation on the electrodes, solvent, and the state of the isotope itself in the solution. In the second, the radiation effects are insignificant and do not affect the state and behaviour of the radioactive isotope.

It must be noted that the following is possible in ultradilute solutions: the formation of radiocolloids, adsorption on the vessel walls and electrodes, interaction of the ions of the radioactive element with contaminants, and the formation from simple ions of more complicated ones, particularly complex ions. In addition, in electrode processes, a radioactive isotope liberated at an electrode covers only part of its surface, and in this connection at concentrations below $10^{-6} M$ the usual electrochemical laws are not always obeyed, for example Nernst's equation having the form

$$\varphi = \varphi_0 + \frac{RT}{zF} \ln \frac{a_1}{a_2} \quad (4.1)$$

where φ is the equilibrium potential at the metal-solution interface, φ_0 is the normal electrode potential at $a_1 = 1$, T is the absolute temperature, z is the charge of an ion in solution, F is the Faraday constant, and a_1 and a_2 are the thermodynamic activities of the ions in the solution and of the element precipitated on the electrode, respectively.

When an ion is precipitated onto the own surface of an element, the quantity a_2 is constant, and Eq. (4.1) is simplified:

$$\varphi = \varphi'_0 + \frac{RT}{zF} \ln a_1 \quad (4.2)$$

where

$$\varphi'_0 = \varphi_0 - \frac{RT}{zF} \ln a_2$$

The Nernst equation (4.2) is observed for ultradilute solutions if an electrode is prepared that is completely coated with the given element. For the concentration in the solution to remain unchanged here, it is necessary to immediately apply a potential to the electrode such that no dissolution of the element deposited on the electrode would occur. This potential is just what corresponds to that calculated by the Nernst equation (4.2).

The electrode material plays an appreciable role in the precipitation process. If the electrode forms no solid solu-

tions or chemical compounds with the precipitating element, and precipitation proceeds in the form of separate aggregates (a sort of microelectrodes, as it were, not differing in their properties from a completely coated electrode), the Nernst equation in its simplest form is obeyed. For observance of the Nernst equation in form (4.2), the thermodynamic activity of the isotope on the electrode must be unity (and the pure substance chosen as the standard state).

It is general knowledge that the total potential jump electrode-solution is determined by the sum of the contributions to the potential of all the electrode processes, among which the potential jump electrode-radioactive isotope at an ultralow concentration is comparatively small. In this connection, the critical potentials of separation of the radioactive isotopes cannot be determined by plotting a current density-voltage curve.

For these purposes, the method of Hevesy and Paneth is used, consisting in determining how the rate of deposition depends on the applied potential, and the method of Ziev, Sinitsina, and Nikolsky, based on measuring the rate of deposition and that of dissolution of the radioactive isotope.

According to the method of Hevesy and Paneth, to find the critical potential of deposition of a radioactive isotope, experimental data are used to plot a curve of the rate of deposition of the isotopes versus the electrode potential (Fig. 4.1). In this case, the rate of deposition is equal or proportional to the density of the current associated with the deposition of only the radioactive isotope. Continuation of the steeply sloping portion of the curve as shown by the dashed line in Fig. 4.1 gives the value of the critical potential φ_{cr} of the isotope at a definite concentration of it in the solution. In a number of cases, the rate of depositing the isotope at a given electrode potential can be determined as the radioactivity of the isotope deposited on the electrode during a selected time interval.

When using the method of Ziev, Sinitsina, and Nikolsky, the critical potential of depositing the radioactive isotope is determined according to the experimental deposition curve and the curve of dissolution of the isotope from the electrode (Fig. 4.2). By connecting these curves with a smooth line (the dashed line in the figure), one finds the critical potential that corresponds to the point of intersection with the axis of abscissas. The method allows the values of the cri-

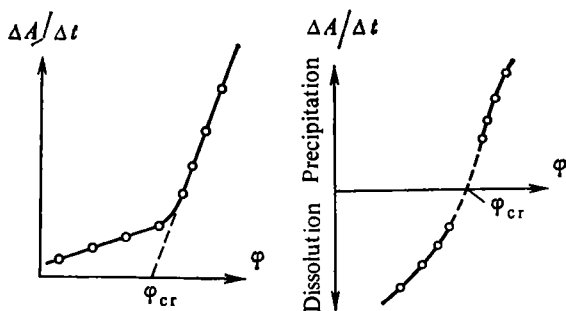


Fig. 4.1. Determination of critical potentials of radioactive isotope separation according to method of Hevesy and Paneth

Fig. 4.2. Determination of critical potentials of radioactive isotope separation according to method of Ziev, Sinitsina, and Nikolsky

tical potentials of isotope deposition to be found with a high accuracy. In addition, here use is made of stabilization of the selected potential on the electrode on which deposition or dissolution of the isotope occurs. The potential is stabilized with the aid of an oxidation-reduction system [for example, $\text{K}_4\text{Fe}(\text{CN})_6\text{-K}_3\text{Fe}(\text{CN})_6$].

Isotopes can be separated in a constant electric field in a gaseous or non-conducting liquid medium. Some radioactive elements are separated by electrochemical displacement on a less noble metal. In this case, it is very convenient to use complexing agents that change the value of the normal potential of the metal, which makes it possible to deposit a less noble metal on it.

In the absence of overvoltage on the electrodes, an element is deposited on the relevant electrode if a potential difference equal to the potential of decomposition of the given salt in a solution appears between the cathode and the anode. The potential of the electrode on which the radioactive isotope is deposited equals the critical potential of deposition at its given concentration. Radioactive isotopes are most often separated from solutions by immersion of two indifferent electrodes in the solution and production of a potential difference greater than the potential of decomposition of the salt in whose form the radioactive isotope is present in the solution.

It is especially convenient to use electrolysis for obtaining and purifying radioactive isotopes without a carrier.

Internal electrolysis can also be used to separate radioactive isotopes. For this purpose, an indifferent electrode is used as the cathode, and a non-indifferent one upon whose solution a potential difference is produced as the anode.

Radioactive isotopes can be deposited on electrodes from a metal with a higher electronegativity. In this "currentless" deposition of the isotope, partial dissolution of the electrode occurs. If electropositive elements are deposited from aqueous solutions in the form of metals, then electronegative metals (for example, rare earth elements) are deposited on the cathode in the form of oxides or hydroxides.

Experiment 4.1. DETERMINING THE CRITICAL POTENTIAL OF DEPOSITION OF RADIOACTIVE ISOTOPES [1, 2]

A. DETERMINING THE CRITICAL POTENTIAL OF DEPOSITING SILVER

The critical potential of ^{111}Ag is determined by a combined method according to the rate of deposition of the radioactive isotope from the solution at preset values of the electrode potential.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A lamp for evaporation. An arrangement for determining the critical potentials of deposition of radioactive isotopes (Fig. 4.3). A platinum cathode and a platinum anode. Beakers for 50 ml (2). Pipettes with syringes for 0.1 and 1 ml. Bowls for measuring the activity.

Radioactive Substances. A solution of 1 M with respect to KNO_3 with pH = 4 or 1 containing ^{111}Ag without a carrier, with an activity of 10^3 cpm/ml.

Reagents. Solutions: 0.25 M $\text{K}_4\text{Fe}(\text{CN})_6$; 0.25 M $\text{K}_3\text{Fe}(\text{CN})_6$; saturated KNO_3 .

Performance of Work

Pour the solution of the radioactive isotope to be studied into a vessel and immerse a platinum plate in the solution as a cathode. Pour a solution containing $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ in an equimolecular proportion into the anode

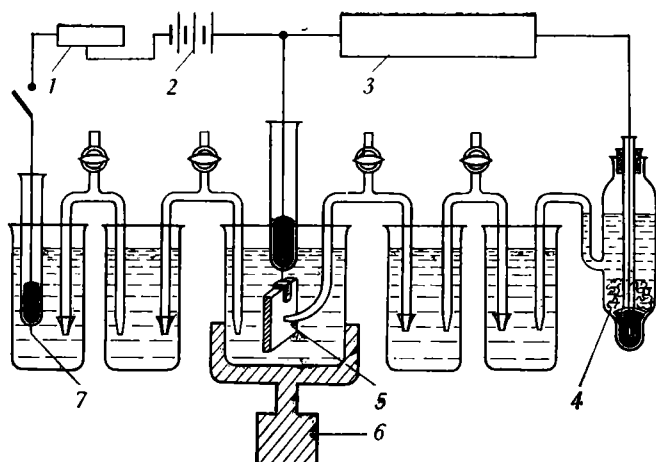


Fig. 4.3. Arrangement for studying the electrochemical separation of radioactive isotopes:
 1—two rheostats; 2—direct current source; 3—high-ohmic potentiometer; 4—calomel electrode; 5—electrode on which isotope is deposited; 6—magnetic stirrer; 7—second electrode (anode)

vessel and immerse a platinum wire anode in it. Connect both electrodes to the working circuit as shown in the diagram (Fig. 4.3). After checking the assembled circuit, switch on the stirrer ensuring agitation of the solution being studied, and feed voltage from direct current source 2 to the electrodes to impart to the cathode the preset value of the potential.

Change the cathode potential or keep it constant during an experiment by changing the resistance of the circuit with the aid of two rheostats 1 (for rough and fine adjustment). Measure the cathode potential with the aid of a conventional compensation circuit with potentiometer 3, using calomel electrode 4 as the reference electrode.

At each given value of the potential, determine the change in the activity of the solution being studied during the same time interval. To do this, take samples of the initial solution and then of the solution after 30 min. Determine the volume of a sample by the activity of the solution, bearing in mind that the activity of preparations being measured must exceed the natural background at least five or six

times. Put the sample into the bowl for measuring activity, evaporate the solution under the lamp, and measure the activity of the dry residue.

Use the data obtained to plot the activity of the radioactive isotope deposited on the cathode (in arbitrary units) during the electrolysis versus the value of the cathode potential.

Calculate the rate of deposition of the radioactive isotope on the electrode (in arbitrary units) for each preset value of the potential according to the amount of isotope deposited on the cathode during a definite period that is the same for all the values of the potential.

According to the data obtained, plot the rate of deposition of the radioactive isotope versus the cathode potential, and, provided that there are sufficient experimental data, find the value of the critical potential of deposition of the isotope in the solution being studied on the given electrode (see Fig. 4.1).

For each preset value of the cathode potential, plot the amount of isotope deposited on the electrode against the duration of electrolysis, calculate the rate of deposition of the isotope on the electrode, appraise the critical potential of the isotope, evaluate the error in measuring the activity, and appraise the accuracy of the results obtained.

B. DETERMINING THE CRITICAL POTENTIAL OF DEPOSITING BISMUTH

Here the task is to study how the critical potential of deposition depends on the concentration of bismuth in the solution. The radioactive isotope ^{210}Bi is used as the radioactive indicator. Graphite is the cathode.

Equipment and Reagents

Equipment and Utensils. An arrangement for studying the electrochemical separation of radioactive isotopes (see Fig. 4.3). A graphite cathode with an area of $(1-2) \times 10^{-4} \text{ m}^2$. A lamp for evaporation. A counter with a detector of β -radiation. A beaker for electrolysis. A beaker for 100 ml. Pipettes with syringes for 0.1 and 1 ml.

Radioactive Substances. A solution of 1 *N* with respect to HNO_3 containing ^{210}Bi with a specific activity of $\approx 2 \times 10^4 \text{ cpm/ml}$.

Reagents. Solution: 10^{-5} M , 10^{-4} M , and 10^{-3} M $\text{Bi}(\text{NO}_3)_3$; 1 *N* HNO_3 , both prepared with doubly distilled water.

Performance of Work

First clean the graphite electrode. For this purpose, wash it with 1 *N* HNO₃, water, and alcohol, and dry it in the air. Pour the 10⁻⁵ *M* solution of Bi(NO₃)₃ into the beaker for electrolysis, and also the solution containing ²¹⁰Bi with a total activity of the indicator of (10-20) × 10³ cpm. Thoroughly stir the solution, and then immerse the graphite electrode in it. Place the beaker with the solution into a sleeve connected to a Warren motor, and immerse the ends of two electrolytic bridges filled with 1 *N* HNO₃ in the solution. (No air bubbles should remain in the bridges.) Connect all the parts of the arrangement (see Fig. 4.3).

Feed to the electrode a potential of 0 ± 0.001 V relative to a saturated calomel electrode (SCE), switch on the agitator, and hold the electrode in this state for one hour*. Next extract the electrode, wash it with water and alcohol, dry it, and measure its activity. Next again immerse the electrode in the solution and feed a potential of 0.2 ± 0.001 V relative to the SCE to it. Keep the electrode at this potential for 20 min (see that the potential remains constant). Then extract it, wash it, and measure its activity. Determine the rate of deposition of the bismuth according to the activity of the ²¹⁰Bi deposited on the electrode during 20 min. Repeat the experiment at a more positive potential (for example, 0.1 ± 0.01 V relative to the SCE). Determine the rate of separation or dissolution. If the deposit dissolved (the activity of the electrode diminished), perform the next separation at a potential of 0.175 ± 0.001 V and so on until the obtained curve of the separation or dissolution of the bismuth versus the electrode potential (see Fig. 4.2) allows the potential to be found at which neither separation nor dissolution of the bismuth is observed. This potential (in the absence of concentration polarization and overvoltage) is the equilibrium one in the given conditions. It is necessary to obtain 5-9 points to plot such a curve.

Perform similar experiments for a 10⁻⁴ and 10⁻³ *M* solution of Bi and find the critical potential of bismuth separation for these concentrations too.

* The preliminary polarization of the electrode at a zero potential relative to the SCE is needed to stabilize the surface of the electrode in the given solution.

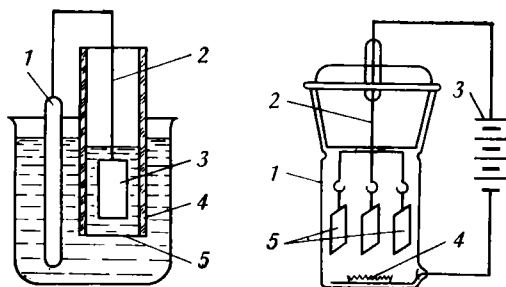


Fig. 4.4. Arrangement for internal electrolysis:
 1—anode (lead or some other metal); 2—platinum wire;
 3—platinum cathode; 4—plastic tube; 5—collodion diaphragm
 (membrane)

Fig. 4.5. Emanator:
 1—emanator casing; 2—cathode; 3—battery; 4—emanating
 substance (for example, RaTh); 5—gold or platinum plates

To verify the applicability of the Nernst equation, plot the critical potential of bismuth separation versus the logarithm of its concentration in the solution.

Experiment 4.2. ELECTROCHEMICAL SEPARATION OF $^{212}\text{Bi}^{3+}$ AND $^{212}\text{Pb}^{2+}$ [3, 4]

To separate the radioactive isotopes of bismuth and lead without a carrier, electrolysis or spontaneous deposition on less noble metals can be used. The standard potential of bismuth is more positive than that of lead, and therefore the bismuth isotopes can be separated from those of lead.

Equipment and Reagents

Equipment and Utensils. An arrangement for internal electrolysis (Fig. 4.4). An emanator with a preparation of RaTh or Th with an activity of 37 MBq (1 μCi) (Fig. 4.5). A counting installation with an end-window counter. Plates of gold [with an area of $(2-3) \times 10^{-3} \text{ m}^2$] and of nickel [$(1-3) \times 10^{-4} \text{ m}^2$]. A tube made from a transparent thermoplastic or polyethylene. A tester. A lamp for evaporation. A porcelain bowl. Beakers for 50, 100, and 500 ml. Bowls for measuring activity. A glass plate $0.1 \times 0.1 \text{ m}$ in size.

Reagents. Collodion. Solutions: 1.5-2 M with respect to NH_4Cl , 0.05 N with respect to HCl , and 7 M with respect to CH_3COOH ; dilute (1 : 1) HNO_3 ; 0.01 N HCl ; transparent thermoplastic (Plexiglas) in dichloroethane.

Performance of Work

(a) Deposition of ^{212}Bi on Platinum by Internal Electrolysis

Prepare a collodion diaphragm. For this purpose, pour out collodion onto a glass surface, wait a while, and then immerse the glass with the collodion film in water—the film readily separates from the glass surface. A collodion film prepared in this way can be preserved in water for two or three days. Cut out from the film with scissors a disk with the diameter of the end of the polyethylene or transparent thermoplastic tube and glue the film disk to the end (dry) of the tube with a solution of Plexiglas in dichloroethane. Assemble the arrangement for internal electrolysis (Fig. 4.4) and check its tightness. Next use the tester to check the connection of the cathode to the anode.

Extract a gold plate from the emanator (Fig. 4.5) and wash off the active deposit (carrier-free ^{212}Bi and ^{212}Pb) with dilute (1 : 1) nitric acid. Evaporate the nitric acid until dry. Wash off the invisible residue containing ^{212}Bi and ^{212}Pb with 2 ml of a solution of 0.05 *N* with respect to HCl , 7 *M* with respect to acetic acid, and 1.5–2 *M* with respect to NH_4Cl . Pour the solution into the cathode space of the arrangement. Immediately pour a solution of the same composition, but without the radioactive isotopes of lead and bismuth, into the anode space of the same arrangement. Place the entire arrangement into a beaker with hot water (60–80 °C). Wait 20–30 minutes. (During this time the maximum amount of ^{212}Bi separates.) Next take apart the arrangement and wash off the ^{212}Bi from the platinum cathode with 2–3 ml of weak nitric or hydrochloric acid. Place the solution into a glass bowl for measuring the activity. Evaporate it until dry under the lamp. Identify the ^{212}Bi by measuring its half-life.

Compare the result obtained with published data (see a table of isotopes) and appraise the purity of the preparation of ^{212}Bi .

(b) Spontaneous Deposition of ^{212}Bi on Metallic Nickel

Extract a gold plate from the emanator (see Fig. 4.5), wash off the active deposit (^{212}Bi and ^{212}Pb without a carrier) with dilute (1 : 1) nitric acid into a beaker, and evaporate

orate the solution of these isotopes until dry. Wash the invisible residue off the beaker with 10 ml of 0.01 *M* HCl. Pour the solution into a 50-ml beaker and immerse a metallic nickel plate in it. The electrochemical deposition of ^{212}Bi should continue for 1-1.5 h. Next extract the nickel plate, dry it with filter paper, and put it on a planchet for measuring radioactivity. Measure the half-life of the separated ^{212}Bi and appraise the purity of the isotope.

Experiment 4.3. ELECTROCHEMICAL SEPARATION OF $^{210}\text{Bi}^{3+}$ AND $^{210}\text{Po}^{4+}$ [2, 4]

The decay of radon leads to the formation of what is called a long-lived active deposit containing ^{210}Pb , ^{210}Bi , and ^{210}Po that are related to one another by a chain of transformations (see the uranium-radium series in Appendix 3).

In the series of potentials, ^{210}Bi and ^{210}Po , and also Ni, Pb, Cu, and Ag are arranged in the following sequence (the values of the standard electrode potentials are indicated in parentheses): Ni(−0.23 V), Pb(−0.13 V), Bi(+0.23 V), Cu(+0.340 V), Po[Po^{4+} – Po^0](+0.77 V), and Ag(+0.80 V).

Polonium is the most electropositive of the three enumerated radioactive isotopes and can be displaced from a solution by many metals. Bismuth can be displaced from a solution freed of polonium by metals to the left of it in the potential series. Since the concentration of the isotope is insignificant, for deposition of the major part of the radioactive isotope, electrodeposition must be carried on for a very long time. To obtain radiochemically pure polonium, it is especially convenient to deposit it on a silver electrode (plate or wire). Deposition is possible in the presence of ions forming complexes with silver, for example chloride ions. The potential of silver in the presence of chloride ions drops to +0.22 V, and of bismuth—to +0.16 V.

Equipment and Reagents

Equipment and Utensils. A counter for registering β -radiation. A counting installation with a scintillation counter for registering α -radiation. A low-speed motor (about 60 rpm). A silver and nickel plates coated on one side with varnish (disks about 20 mm in diameter). A glove box for work with α -active isotopes. A lamp for evaporation. A centrifuge. A quartz or platinum bowl. Beakers for 20 and 50 ml. Bowls for measuring activity.

Radioactive Substances. A solution of a long-lived active deposit of radon (equilibrium amounts of ^{210}Pb , ^{210}Bi , and ^{210}Po), 0.4 *N* with respect to HCl, with a specific β -activity of 500 cpm/ml.

Reagents. Alcohol. Acetone. Crystalline $\text{Pb}(\text{NO}_3)_2$. Solutions: dilute (1 : 3) HNO_3 ; 2 *N*, 0.1 *N*, and concentrated HCl.

Performance of Work

Perform all the work in a glove box for work with α -active isotopes. Before beginning work, see that all the required isotopes and utensils are inside the box, otherwise introduce everything needed through the prechamber and close the chamber. The doors of the prechamber must be closed during work.

(a) Separation of ^{210}Po

Place 5-10 ml of a solution containing equilibrium amounts of ^{210}Pb , ^{210}Bi , and ^{210}Po (a solution of 0.4 *N* with respect to HNO_3 and 0.1 *N* with respect to HCl) into a 20-ml beaker. Fasten the silver plate to the motor axle and immerse it in the radioactive solution. Preliminarily degrease the plate by immersing it for a short time in a solution of HNO_3 (1 : 3).

Deposit the ^{210}Po on the silver electrochemically for two or three hours with constant rotation of the electrode. Next extract the silver plate, rinse it in a beaker with alcohol or acetone and place it in a bowl for measuring activity. Carefully extract the preparation for measuring the activity (the silver plate in the glass bowl) through the prechamber, seeing that the door of the glove box is closed when the preparation is being extracted from the prechamber. Close the door of the prechamber and measure the activity of the preparation. Use the counter for registering β -radiation to see that there is no β -activity in the specimen, and measure the α -activity with the α -scintillation counter. By determining the path of the α -particles, identify the ^{210}Po . Repeat the measurements in 8-12 days.

To prepare a polonium solution, dissolve the silver plate with the polonium deposited on it in a few millilitres of dilute (1 : 3) nitric acid. Dilute the solution with water and precipitate the silver with an excess of 2 *N* HCl. Separate the silver chloride precipitate by centrifuging. Evaporate the solution until dry in a quartz or platinum bowl. Dissolve the residue containing polonium in 0.1 *N* HCl.

(b) Separation of ^{210}Bi

Evaporate the solution purified of polonium until dry. Dissolve the invisible precipitate in 0.1 *N* hydrochloric acid, pour over the solution into a beaker and immerse in it the nickel plate fastened to the motor axle. Deposit the ^{210}Bi during 4-6 h with rotation of the nickel plate. It is good to add 2-5 mg of any lead salt to the solution to reduce the deposition of the ^{210}Pb on the electrode. Next extract the plate, rinse it in water and alcohol, place it into a glass bowl, and remove it from the glove box through the prechamber. Check for the presence of polonium with the α -scintillation counter. By immersing the nickel plate in hot concentrated hydrochloric acid,^f wash off all the ^{210}Bi . Prepare the substance for measuring its activity by carefully evaporating the solution in a glass bowl. By measuring the half-life of the ^{210}Bi , prove that the preparation contains no ^{210}Pb .

Experiment 4.4. SEPARATION OF ^{90}Y FROM ^{90}Sr BY ELECTROLYSIS [2]

In the β -decay of ^{90}Sr , the daughter β -active isotope ^{90}Y is formed. The standard electrochemical potential of both yttrium and strontium is appreciably more negative than that of hydrogen. This is why metallic yttrium and strontium cannot be obtained from aqueous solutions of compounds of Y^{III} and Sr^{II} . But at a high current density, ^{90}Y without a carrier is deposited on a cathode in the form of its oxide or hydroxide from weak nitric or hydrochloric acid solutions. The isotope ^{90}Sr is deposited on a cathode in the form of its carbonate from neutral or weakly alkaline solutions when carbon dioxide is continuously passed through them.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window β -counter or a scintillation counter. Aluminium screens of various thickness. An arrangement for electrolysis (Fig. 4.6). A Kipp gas generator for producing carbon dioxide. A water bath. A cylinder with nitrogen. A lamp for evaporation. Beakers for 50 ml (3). Pipettes for 1 and 5 ml with syringes. Bowls for measuring activity.

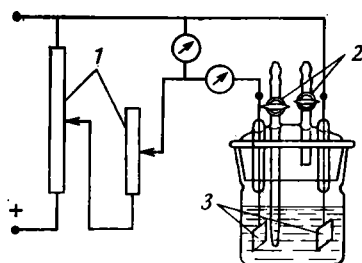


Fig. 4 6. Arrangement for electrolysis:
1—rheostats; 2—cocks; 3—platinum electrodes

Radioactive Substances. A solution in 0.01 *M* nitric or hydrochloric acid containing $^{90}\text{Sr}^{2+}$ and $^{90}\text{Y}^{3+}$ with a specific activity of 10^4 – 10^5 cpm/ml.

Reagents. Acetone. Solutions: 0.01 *N* and 5 *M* HNO_3 (or HCl); 0.1 *M* NH_4OH .

Performance of Work

Assemble the arrangement for electrolysis (Fig. 4.6). Pour 1 ml of an active solution into a beaker and dilute it to 5 ml with 0.01 *M* nitric or hydrochloric acid. Put the beaker in a water bath with a temperature of 55–65 °C. Perform electrolysis during 30–40 min at a current density of about 700 A/m² and a voltage across the electrodes of about 15 V. Pass a stream of nitrogen or air through the solution. Without stopping the current through the electrolyzer, extract the platinum cathode, rinse it twice with acetone, and, after switching off the current, immerse it in a beaker with 5 *M* nitric or hydrochloric acid. Evaporate the solution obtained containing ^{90}Y until dry in a bowl for measuring activity under a lamp.

Neutralize the solution in the electrolyzer with ammonia to a neutral reaction using a universal indicator. Lower the cathode into the solution. Perform electrolysis during 30–40 minutes at a current density of 750–1000 A/m² and a voltage of 18 V. During electrolysis, pass an intensive stream of carbon dioxide through the solution and maintain its temperature at 55–65 °C. Next, without removing the voltage, extract the electrode, rinse it twice with acetone, wash off the invisible deposit of ^{90}Sr with 5 *M* hydrochloric or nitric acid into a bowl for measuring activity and evaporate the solution containing ^{90}Sr until dry.

Determine the maximum energies of the β -particles of the ^{90}Sr and ^{90}Y preparations by measuring the absorption of the β -rays in aluminium. Measure the decay of the ^{90}Y and its accumulation in the preparation of ^{90}Sr . Determine the half-life of the ^{90}Y . Compare the obtained values with published data and make conclusions on the purity of the preparations of ^{90}Sr without ^{90}Y and of ^{90}Y .

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Chapter 5 State of Radioactive Isotopes in Ultradilute Solutions

THEORETICAL INTRODUCTION [1]

The radioactive isotopes of the natural radioactive elements (except uranium and thorium) are encountered in nature in ultrasmall concentrations; in nuclear transformations ultradilute systems containing artificially radioactive isotopes are also obtained.

In connection with the development of nuclear power engineering, radioactive isotopes—the products of fission of uranium and the products of structural material corrosion—have appeared in the water of rivers, seas, and oceans. The process of separating radioactive isotopes is associated with a knowledge of the physicochemical state and the behaviour of substances in ultradilute solutions. Separation quite often terminates in the obtaining of strongly dilute solutions—solutions of radioactive isotopes without a carrier. Radioactive elements with small half-lives (such as francium

and astatine) cannot be prepared in weighable amounts. Therefore, when working with such substances, one always has to do with ultradilute solutions. If the concentration of a radioactive isotope of a given element is below 10^{-6} - 10^{-7} mol/litre (ultradilute solutions), its behaviour in various physicochemical processes may greatly differ from the behaviour of the element at higher concentrations.

Radioactive isotopes may be found in solutions in the molecular, ionic (simple and complex ions) and colloidal states. In other words, many forms of a radioactive isotope may coexist in a definite solution. The ratio between the different forms of a given isotope depends on the nature and degree of purification of the solvent, the pH of the medium, the presence of complexing substances, the ionic strength of the solution, the temperature, and the retention time.

Radioactive isotopes may form true or pseudocolloids (adsorption colloids). To assay the nature of colloid formation (true or pseudocolloids on a silica acid gel), the Starik criterion is used [2]. According to this criterion, a radioactive isotope forms true colloids if the maximum of the manifestation of colloidal properties is at larger pH's of the solution than the maximum adsorption on glass.

If an exceedingly poorly soluble compound forms in a solution of a radioactive isotope (the solubility product P_s is satisfied when salts or hydroxides form), the formation of small aggregates of the solid phase is possible. Such aggregates consisting only of a compound of a radioactive isotope form a true colloidal solution of the radioactive isotope. For each element, however, a definite minimum concentration of it is needed for the formation of the solid phase, therefore the formal achievement of the magnitude of the solubility product is still insufficient for a precipitate of the element to form.

The most minute dust particles are always present in any solvent. In addition, finely dispersed colloidal solutions of silicic acid form (owing to its leaching out from the walls of glassware). Ionic and molecular forms of a radioactive isotope are deposited on these solid particles as a result of ion exchange and molecular adsorption. A pseudocolloidal solution of the radioactive isotope forms. In a number of cases, by studying adsorption, electrodialysis, electrophoresis, diffusion, and other phenomena, we can determine the state of a

carrier-free radioactive isotope in a given solution and, consequently, predict its behaviour in various chemical processes.

Experiment 5.1. INVESTIGATION OF STATE OF RADIOACTIVE ISOTOPES IN SOLUTIONS

Radioactive isotopes may be in solutions in the form of ions, molecules, and colloidal particles. A collection of methods based on the phenomenon of sorption, electrodialysis, diffusion, and electrophoresis is used in the experiment to study the distribution of radioactive isotopes according to the forms in which they occur in solutions.

A. METHOD OF ADSORPTION ON GLASS

The sorption coefficient depends on the charge, the polarizability, and the hydration of ions, and for hydrolyzing ions — on the degree of hydrolysis and the presence of molecular and colloidal forms. In connection with the fact that equilibrium sets in slowly between various forms of a radioactive isotope, aged solutions are studied.

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter or a β -scintillation detector and a detector of γ -radiation. A pH meter and universal indicator paper. Warren motors for 60 rpm. Beakers for 50 ml. Glass disks 2 cm in diameter with a prolongation. Bowls and counter planchets for measuring radioactivity. Watch glasses and a crystallizer with a cover glass.

Radioactive Substances. Solutions of 5 N HCl containing ^{137}Cs , ^{88}Sr , ^{144}Ce , ^{59}Fe , and ^{95}Zr without a carrier, with a specific activity of 10^5 – 10^6 cpm/ml.

Reagents. 0.1 N NaOH, 0.1 N HCl.

Performance of Work

Pour a dose of 20 ml of distilled water into each of the 50-ml beakers and introduce an amount of the radioactive isotope such that the specific activity of the solution will be 10^4 cpm/ml. Use the NaOH and HCl solutions to establish the pH (from 1 to 10). Cover the beakers with the watch glasses, place them into the crystallizer, and cover it with a glass to prevent contamination. After this, let it stand for

several days. Next thoroughly clean the glass disks with the aid of the concentrated HCl, degrease them with benzene, wash them with alcohol (acetone) and water, connect them to the Warren motors, and immerse them in the beakers.

After a definite stirring time (20 min), extract each disk, wash it in a beaker containing HCl with the same pH for a few seconds, dry it in the air, and measure its radioactivity. Immerse the disk again in the solution, and measure its radioactivity in one hour. Repeat the operations in two hours. The equilibrium sorption coefficient is calculated by the formula

$$K = \frac{I_d V}{S I_{\text{sln}}} \times 100\%$$

where I_d is the radioactivity of the disk, I_{sln} is the radioactivity of the solution, S is the surface of the disk, cm^2 , and V is the volume of the solution, ml.

Plot K versus the pH. Compare the curves showing how the sorption coefficients depend on the pH for the isotopes of hydrolyzing and non-hydrolyzing elements. Arrive at a conclusion on the probability of colloid formation.

Obtain additional information on the state of the radioactive isotopes from data on the kinetics of desorption in solutions of acids and salts.

Compare the results of the experiment with the data obtained in determining the fraction of the colloidal forms of a radioactive isotope (see Sec. B of the present experiment).

B. METHOD OF ELECTRODIALYSIS

The use of the method of electrodialysis makes it possible to determine the sign of the charge of particles, appraise their dimensions, and in a number of cases—the fraction of the radioactive isotope in the colloidal form.

Equipment and Reagents

Equipment and Utensils. A five-section electrodialyzer with cellophane membranes. A voltmeter for measuring d-c voltage (100 V), a milliammeter (from 1 to 100 mA). Two rheostats with resistances of 1 k Ω and 300 Ω . Beakers for 200 ml. Watch glasses. A crystallizer with a cover glass. Bowls and planchets for measuring radioactivity. A counter with β - and γ -scintillation detectors. Pipettes for taking samples (3) for 1 ml.

Radioactive Substances. Solutions of 5 *N* HCl containing carrier-free ^{137}Cs , ^{89}Sr , ^{144}Ce , ^{59}Fe , and ^{95}Zr with a specific activity of 10^5 cpm/ml.

Reagents. 0.1 *N* HCl and 0.1 *N* NaOH.

Performance of Work

Before beginning work, check the tightness of the device and the membranes. Fill the device with distilled water. Pour 10 ml of distilled water into each of the 20-ml beakers, and dose the solutions containing the radioactive isotopes so that the specific radioactivity is 10^4 cpm/ml. Use the solutions of 0.1 *N* HCl and 0.1 *N* NaOH to set the pH within the range from 3 to 10. Cover the beakers with the watch glasses, and place them into the crystallizer for equilibrium to set in between the various chemical forms of a radioactive isotope. Cover the crystallizer with its glass. After several days, transfer the solutions one by one into the middle part of the electrodialyzer, supply a voltage corresponding to a current through the device of not over 50 mA, and after definite time intervals take 0.1-ml samples from the middle part, the catholyte, and the anolyte. (Take the first samples in 10-20 min.)

Use the results of measuring the radioactivity of the samples to plot the radioactivity of the solutions in the three sections of the electrodialyzer against the duration of the process at a given pH, and then the rate of electrodialysis against the pH. Arrive at a conclusion on the fraction of charged and neutral forms of the radioisotope. Upon completing work, deactivate the device, wash it with water, and let it stand with its sections filled with distilled water. It is good practice to perform an experiment with one isotope and at a pH of 3, 5, 7, and 9 (2, 4, 6, and 8).

C. DETERMINING THE DIFFUSIVITY, SIZE, AND MOLECULAR MASS OF PARTICLES

Measurement of the diffusivity allows one to evaluate the radius of particles by using the Einstein-Smoluchowski formula:

$$r = \frac{RT}{6\pi N_A} \cdot \frac{1}{\eta D}$$

where N_A is the Avogadro constant, η is the dynamic viscosity of the medium (N·s)/m², and D is the diffusivity, m²/s. The molecular mass of particles can be appraised by Einstein formula

$$M = \frac{60}{D^2}$$

For water, $\eta = 0.001$ (N·s)/m², and $r = 2.1 \times 10^{-13}/D$.

The diffusivity is determined by the method of outflow from a capillary as described in Experiment 18.5 (Vol. 2). Aqueous solutions of HCl and NaOH are used as the medium at a pH corresponding to the acidity of the aged solutions of the radioisotopes.

Equipment and Reagents

Equipment and Utensils. A device for determining the diffusivity, a set of capillary tubes. Bowls or planchets for measuring radioactivity. A counter with β - and γ -scintillation detectors. Microtest tubes for 1 ml. Micropipettes.

Radioactive Substances. Solutions of 5 N HCl containing the radioactive isotopes ¹³⁷Cs, ⁸⁹Sr, ¹⁴⁴Ce, ⁵⁹Fe, and ⁹⁵Zr with a specific radioactivity of 10⁶ cpm/ml.

Reagents. 0.1 N HCl and 0.1 N NaOH.

Performance of Work

Prepare solutions of the radioactive isotopes at a pH from 1 to 10 with a specific radioactivity of about 10⁵ cpm/ml in the 1-ml microtubes. Put the tubes into a beaker, cover the latter with a watch glass, and let it stand for several days. Determine the diffusivity according to the description in Experiment 18.5 (Vol. 2). Calculate the radius of the particles and their molecular mass. Plot r and M against the pH for each isotope. Compare the data obtained with the results of the preceding experiments.

D. METHOD OF ELECTROPHORESIS

The method of electrophoresis can be used for a qualitative appraisal of the ratio between positively and negatively charged particles in solutions.

Quantitative data on the ratio between the forms can be obtained upon introducing corrections for their mobility provided that there is no dissociation of the neutral molecules in equilibrium with the ionic part.

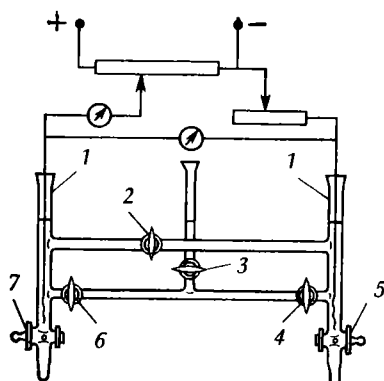


Fig. 5.1.

Arrangement for electrophoresis:

1—electrodes (platinum wire); 2-7—cocks

Equipment and Reagents

Equipment and Utensils. An arrangement for electrophoresis. A voltmeter and an ammeter for measuring the parameters of a direct current (for 100 V and 50 mA). Rheostats for 1 k Ω and 500 Ω . A counter with β - and γ -scintillation detectors. Beakers for 10 ml, watch glasses, a pipette for 3 ml. Bowls and planchets for measuring radioactivity.

Radioactive Substances. A set of radioactive isotopes as in Sec. A or B.

Reagents. 0.1 N HCl and 0.1 N NaOH.

Performance of Work

Keep the solutions of the radioactive isotopes for several days at a pH from 2 to 10 in the beakers covered with watch glasses, and then perform electrophoresis of the solutions. For this purpose, fill the middle part of the electrophoresis arrangement with a radioactive solution via the tube with cock 3 (Fig. 5.1) (cocks 4 and 6 are closed). Next open cocks 4 and 6 in turn until the solution gets into the openings of their stoppers. With cocks 4 and 6 closed, pour a solution with the same pH, but containing no radioactive isotope (cocks 5 and 7 are closed) into the side parts of the arrangement. Use cock 2 to make the levels in the elbows equal. See that there are no air plugs in the arrangement.

Immerse lengths of a platinum wire into the side parts of the arrangement and connect them to a d-c source at 100 V.

Close cocks 2 and 3 and open 4 and 6. Perform electrophoresis at a constant current of 5-10 mA for 30 min. Switch off the current and pour all the liquid from the elbows into two test tubes for measuring activity after first closing cocks 4 and 6. Find the ratio of the activities of the cationic I_c and anionic I_a parts of the arrangement.

The quantities obtained characterize the fraction of a radioactive isotope in the investigated solutions in the form of cations and anions. Plot I_c/I_a against pH. Compare the results of the experiment with the preceding investigations.

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Chapter 6 Isotope Exchange

THEORETICAL INTRODUCTION [1]

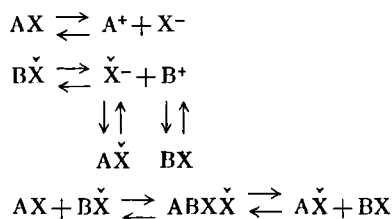
By isotope exchange is meant the redistribution of atoms of the isotopes of a given element inside a molecule, between different molecules or phases that does not lead to other chemical or physicochemical changes in the system. Isotope exchange may be simple and complicated. In simple exchange, all the atoms of a given element enter the exchange at the same rate. In complicated exchange, atoms of the given element participate that are in various energy states or in various positions in a molecule, as a result of which the rate of exchange is not the same for such atoms. In this chapter, we shall deal with the laws (kinetics) of only simple isotope exchange.

Isotope exchange is widely used in applied radiochemistry for studying the mechanism of chemical reactions, the mobility of atoms in molecules, the structure and chemical composition of compounds, for determining the surface

of crystals, measuring saturated vapour pressure, self-diffusivity, etc.

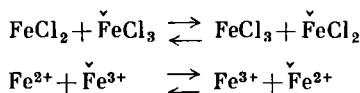
If isotope exchange occurs between the components of a system being studied by the method of radioactive tracers, and its rate is higher than or commensurable with the rate of the process being studied, the method of radioactive tracers cannot be used. On the other hand, the separation of carrier-free radioactive isotopes by the method of recoil nuclei (see Chap. 7) or enrichment is impossible if isotope exchange occurs between the irradiated and separated compounds.

Isotope exchange takes place if the participating compounds experience thermal or electrolytic dissociation (sometimes the dissociation of one of the compounds is sufficient) or form an intermediate complex. In these cases, exchange occurs via the reversible chemical reactions:

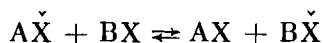


Other paths of isotope exchange are possible, also associated with the presence of reversible chemical reactions.

Isotope exchange is possible between two compounds containing a given element in various oxidation states by the transfer of an electron, actually without the movement of the atoms:



The **equilibrium constant** of an isotope exchange reaction proceeding according to the equation



is:

$$K_{eq} = \frac{[AX][B\check{X}]}{[A\check{X}][BX]} \approx 1 \quad (6.1)$$

An exception is the exchange of light element isotopes, for which it may differ considerably from unity.

The **degree or fraction of exchange** F is a measure of reaction approaching equilibrium:

$$F = \frac{S_B - S_{B,0}}{S_{B,\infty} - S_{B,0}} = \frac{S_A - S_{A,0}}{S_{A,\infty} - S_{A,0}} \quad (6.2)$$

where $S_{B,0}$, S_B , and $S_{B,\infty}$ are the specific radioactivity of the component $B\check{X}$ initially, at the instant t , and in equilibrium, and $S_{A,0}$, S_A , and $S_{A,\infty}$ are the relevant specific radioactivities of the component $A\check{X}$. If at the initial instant $S_{B,0} = 0$, we have

$$F = \frac{S_B}{S_{B,\infty}} \quad (6.3)$$

We distinguish **homogeneous** isotope exchange proceeding between substances in one phase, and **heterogeneous** exchange proceeding between two different phases. The degree of homogeneous isotope exchange F is associated with the rate of exchange by the equation

$$-\ln(1 - F) = \frac{a+b}{ab} wt \quad (6.4)$$

where a and b are the sums of the concentrations of the molecules $\{AX\} + \{A\check{X}\}$ and $\{BX\} + \{B\check{X}\}$, respectively, w is the rate of isotope exchange (it is constant at a constant concentration of the reactants), and t is the duration of exchange.

The rate of homogeneous isotope exchange is

$$w = ka^n b^m \quad (6.5)$$

where k is the exchange rate constant (a quantity not depending on the concentration of the reacting molecules).

To determine the order of a reaction of homogeneous isotope exchange, i.e. the sum of the exponents n and m , we must use experimental data to plot $\log w$ against $\log a$ or against $\log b$ at a constant b or a , respectively. The slope of the straight line to the axis of abscissas will equal the quantities n and m , respectively.

The order of a homogeneous isotope exchange reaction can also be determined according to the **half-time of exchange** $t_{1/2}$, the time in which F becomes equal to $1/2$.

If the half-time of exchange does not depend on the concentration of the forms being exchanged, a first-order reaction proceeds. If the half-time of exchange is inversely proportional to the sum of the concentrations of the molecules being exchanged, a second-order reaction proceeds.

Having determined the order of a reaction according to the experimental data, use formula (6.5) to evaluate the exchange rate constant at the given temperature.

The activation energy of isotope exchange is calculated by the Arrhenius equation

$$k = pZe^{-E/RT} \quad (6.6)$$

where p is a steric factor, Z is the number of collisions, and E is the activation energy of the isotope exchange reaction. In the logarithmic form, Eq. (6.6) transforms into an equation of a straight line:

$$\ln k = \ln (Zp) - \frac{E}{RT} \quad (6.7)$$

If we determine the value of k for different temperatures and plot $\log k$ versus $1/T$, the straight line obtained will intercept $\log (pZ)$ on the axis of ordinates, while the slope of the line with respect to the axis of abscissas gives the quantity $0.4343E/R$.

The laws of heterogeneous isotope exchange, if the rate of diffusion in both phases is much higher than the rate of exchange, remain the same as for homogeneous isotope exchange. The same laws are observed if when diffusion is virtually absent in one of the phases, there are many atoms being exchanged on its surface, and relatively few in the other phase, for example, finely dispersed precipitates in greatly dilute solutions.

The degree of exchange in this case can be found from the equation:

$$-\ln (1 - F) = \frac{N_s + N_{sln}}{N_s N_{sln}} N' t \quad (6.8)$$

where N_s and N_{sln} are the number of exchanging atoms on the surface of the solid phase and in the solution, N' is the rate of exchange, atom/s, and t is the exchange time.

The half-time of exchange is:

$$t_{1/2} = \frac{0.693 N_s N_{\text{sln}}}{N' (N_s + N_{\text{sln}})} \quad (6.9)$$

If the rates of exchange and diffusion are commensurable, the equations become more intricate.

Experiment 6.1. ISOTOPE EXCHANGE OF LEAD BETWEEN $\text{Pb}(\text{NO}_3)_2$ AND PbCl_2 IN A SOLUTION [2]

Isotope exchange in solutions of electrolytes is achieved via the dissociation of both components.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. An analytical balance. A drying cupboard. An emanator with a preparation of RdTh — 5×10^2 MBq (10-20 mCi) of ^{228}Th and a platinum, gold, or tantalum plate. A porcelain bowl. A crystallizer. Beakers for 100 ml (2). A micropipette with a syringe. Cylinders for 20 ml (2). Funnels for preparing precipitates for measurement (2). A glass rod. Watch glasses (2).

Reagents: $\text{Pb}(\text{NO}_3)_2$, PbCl_2 . Solutions: 1 and 0.1 N HNO_3 , concentrated HCl .

Performance of Work

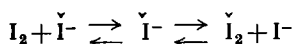
Expose the platinum plate during one day in the emanator under a hood. Transfer the plate with pincers into the porcelain bowl. Next wash off the active deposit of thoron from the plate with 10 ml of 1 N nitric acid to which several milligrams of $\text{Pb}(\text{NO}_3)_2$ have been added with heating in the porcelain bowl. Evaporate the solution until dry on a water bath, dissolve the content of the bowl in 10 ml of distilled water, pour it over into a graduated cylinder and add water to 20 ml. Add an aliquot part of the solution to a solution of 1.75 g of $\text{Pb}(\text{NO}_3)_2$ in 75 ml of distilled water in a beaker. Add 1.5 g of PbCl_2 to the obtained active solution of $\text{Pb}(\text{NO}_3)_2$ with boiling. Cover the beaker without fail with a watch glass. After dissolving of the PbCl_2 , transfer the beaker with the solution from the stove to a bowl with cold water prepared beforehand. Stir the solution and after complete precipitation of PbCl_2 crystals from it, filter them in a special funnel. Preliminarily weigh the filter. Transfer the PbCl_2

crystals that have adhered to the walls, using a minimum amount of cold water, with the rod onto the filter. Dry the precipitate on the filter at 100-110 °C in the drying cupboard and weigh it together with the filtrate. Transfer the filtrate to a beaker and evaporate it up to its previous volume (~75 ml). Add 2 ml of concentrated hydrochloric acid to the evaporated solution. Cool the beaker by placing it in a bowl with water, and transfer the precipitate, as in the first case, onto a filter, dry and weigh the filter with the precipitate.

In 3-4 hours, when an amount of ThC close to equilibrium accumulates from the ThB, measure the activity of both precipitates in the counter with the detector of β -radiation. The measurement may be performed directly on the filters or in any other way, taking a known weight amount of the precipitate. Calculate the specific activity of both preparations, and the degree of exchange by formula (6.3).

Experiment 6.2. ISOTOPE EXCHANGE OF IODINE BETWEEN I_2 AND NaI IN A SOLUTION [3]

The isotope exchange of iodine between an aqueous solution of iodine and sodium iodide proceeds at a high rate via the formation of an intermediate complex. Equilibrium is achieved virtually instantaneously:



Equipment and Reagents

Equipment and Utensils. A counter with a detector of β - or γ -radiation. A water bath. A funnel for preparing precipitates for measurement. A porcelain bowl. A measuring cylinder for 100 ml. A pipette with a syringe for 1 ml. Beakers for 100 ml (2).

Radioactive Substances. A solution of NaI containing ^{131}I with a concentration of 3 g/litre and a specific activity of 1000 cpm/ml.

Reagents. Solutions: I_2 with a concentration of 254 mg/litre: 0.5 N HNO_3 ; 0.05 M $AgNO_3$.

Performance of Work

Pour 100 ml of a 0.002 M solution of iodine into the porcelain bowl and add 1 ml of the active 0.02 M solution of NaI (1000 cpm/ml) containing ^{131}I . Evaporate the solution on the water bath until dry. Dissolve the residue in water

and transfer it into a beaker. Pour 1 ml of the active solution of NaI into the second beaker and dilute it with water up to a volume equal to that in the first beaker. Precipitate AgI from both solutions after first acidifying them with 1 ml of 0.5 *M* nitric acid. Separate the precipitates on the funnel for preparing precipitates (see Fig. 0.16, p. 63).

Measure and compare the activity of the precipitates. Assay the degree of iodine exchange.

Experiment 6.3. ISOTOPE EXCHANGE OF THALLIUM BETWEEN COMPOUNDS OF Tl^+ AND Tl^{3+} IN A SOLUTION [4-6]

The task of this experiment is to study the kinetics of isotope exchange of thallium between compounds of the mono- and trivalent element, which proceeds according to the electron transfer mechanism.

A. ISOTOPE EXCHANGE OF THALLIUM BETWEEN $TlClO_4$ AND $Tl(ClO_4)_3$ IN A PERCHLORATE SOLUTION

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. An arrangement for conducting isotope exchange. A thermostat. A drying cupboard. An analytical balance. Pipettes for 50 and 2 ml with syringes. Test tubes for 10 ml (10). A funnel for preparing precipitates for activity measurement.

Radioactive Substances. A 0.0244 *M* solution of $TlClO_4$ in 1.5 *M* $HClO_4$ containing ^{204}Tl with a specific activity of 2×10^3 cpm/ml.

Reagents. Solutions: 0.0244 *M* $Tl(ClO_4)_3$ in 1.5 *M* $HClO_4$; 2 *M* NaBr.

Performance of Work

Perform the isotope exchange at room temperature. Pour 50 ml of a 0.0244 *M* solution of $TlClO_4$ in 1.5 *M* $HClO_4$ containing ^{204}Tl and the same amount of a 0.0244 *M* solution of $Tl(ClO_4)_3$ in 1.5 *M* $HClO_4$ into the arrangement for conducting isotope exchange. Determine the initial activity immediately after stirring, and then again determine the activity of the Tl^+ in the solution during three days, approximately after 4, 20, 44, and 70 hours. Take two 2-ml samples of the solution for each measurement. Precipitate

the Tl^+ , adding 2 ml of a 2 *M* solution of NaBr; take the time of precipitation as the end of the exchange time. Let the precipitate of TlBr settle exactly 5 min, and then transfer the solution with the precipitate onto a weighed filter placed in the funnel for preparing precipitates for measurement. Begin sucking off of the solution in exactly 5 min after its transfer to the filter. Wash the precipitate with a small amount of water (5 ml) to remove the perchloric acid.

Dry the samples at a temperature of 100-110 °C during one hour, weigh them, and measure their activity in the counting installation with the end-window counter, introducing a correction for self-absorption. Enter the obtained data into a table with the following form:

Sample No.	Time of taking sample, h	Mass of precipitate, mg	Activity of precipitate, cpm	Specific activity, cpm/mg	Correction for self-absorption of radiation	Corrected specific activity, cpm/mg

Evaluate the degree and rate of exchange. Plot $\log (1 - F)$ against t and find the half-time of exchange.

Perform similar experiments at various temperatures (35, 45, and 60 °C) in thermostatted conditions: again evaluate the degree and rate of exchange, the half-time of exchange, the rate constant of exchange, and determine the exchange activation energy.

B. ISOTOPE EXCHANGE OF THALLIUM BETWEEN Tl_2SO_4 AND $\text{Tl}_2(\text{SO}_4)_3$ IN A SULPHURIC ACID SOLUTION

Equipment and Reagents

Equipment and Utensils. A counting installation with an end-window counter. An arrangement for conducting exchange. A thermostat. A drying cupboard. An analytical balance. A pipette for 5 ml. Measuring cylinders for 50 and 10 ml. Beakers for 100 ml (6). A crystallizer. A funnel for preparing precipitates for measurement.

Radioactive Substances. A 0.01 *M* solution of $\text{Tl}_2(\text{SO}_4)_3$ in 2 *N* H_2SO_4 containing ^{204}Tl with a specific activity of 2×10^3 cpm/ml.

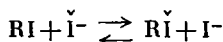
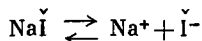
Reagents. A 0.01 *M* solution of Tl_2SO_4 in 2 *N* H_2SO_4 ; 0.25 *M* K_2CrO_4 , 1 *N* NaOH, 1 *M* KCN, and 7 *M* NH_4OH .

Performance of Work

Pour 50 ml of a 0.01 *N* solution of Ti_2SO_4 in 2 *N* H_2SO_4 into the arrangement for conducting exchange placed in a thermostat at 20 °C, and after the required temperature is established add 50 ml of a 0.01 *M* solution of $\text{Ti}_2(\text{SO}_4)_3$ in 2 *N* H_2SO_4 labelled with ^{204}Ti . Immediately after stirring, take 5 ml of the mixture. Next take samples after every 10 min during one hour and after every 20 min during 1.5 h more. Directly after taking a sample, precipitate the Ti^+ in the form of its chromate with an equimolecular amount of a reagent having the composition: 0.25 *M* K_2CrO_4 , 1 *N* NaOH , 1 *M* KCN , and 7 *M* NH_4OH with cooling and stirring during 10-15 min. Filter the precipitate on the weighed filter of the funnel for preparing precipitates for measurement, wash it with a small amount of cold water, dry and weigh it, and measure its activity in the counting installation with the end-window counter. Introduce corrections for self-absorption. Enter the results in a table similar to that given in Experiment 6.3A. Plot $\log (1 - F)$ versus *t* and use it to find the half-time of exchange.

Experiment 6.4. ISOTOPE EXCHANGE OF IODINE BETWEEN RI AND NaI IN AN ALCOHOL SOLUTION [7]

Exchange between alkyl iodide and sodium iodide in a solution proceeds via dissociation of the sodium iodide:



It is convenient to study this reaction in a solution of ethyl alcohol (boiling at 78.3 °C). The rate of the reaction can be calculated proceeding from a bimolecular mechanism.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of γ -radiation [a crystal of $\text{NaI}(\text{Ti})$ with a well]. A balance. An arrangement for studying isotope exchange (Fig. 6.1). A pipette for 3 ml with a syringe. A graduated cylinder for 50 ml. Beakers for 100 ml with a watch glass (6). Separatory funnels for 50 ml (3). Test tubes for measuring γ -activity (10). A conical funnel. Measuring flasks for 25 ml (2).

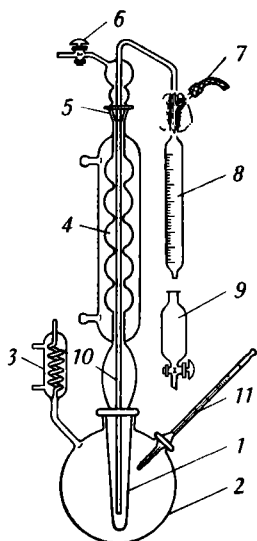


Fig. 6.1.

Arrangement for studying isotope exchange:

1—reaction flask; 2—thermostat with a liquid boiling at a constant temperature; 3, 4—coolers; 5—ground-glass joint; 6—cock; 7—branch tube; 8—pipette; 9—separatory funnel; 10—tube for taking samples; 11—thermometer

Radioactive Substances. A carrier-free aqueous solution of Na^{131}I with a specific activity of at least 10^8 cpm/ml.

Reagents. NaI ; ethyl iodide with a known density; benzene; water; alcohol (50 ml/experiment); ice.

Performance of Work

Before beginning work, acquaint yourself with the arrangement for studying isotope exchange; bring out the thermostat of the reaction flask to the preset temperature conditions. Check the calibration of the sampling pipette, and if necessary calibrate it with the aid of the micrometric screw.

Prepare a 0.2 *M* ethanol solution of sodium iodide containing ^{131}I with a specific activity of 10^8 cpm/ml and a 0.2 *M* ethanol solution of ethyl iodide in the 25-ml flasks.

Use the conical funnel to simultaneously pour the contents of both flasks into the reaction flask of the arrangement via the small cooler. Directly after filling the arrangement, take the first sample with the pipette ($t = 0$). Next

take samples in 15, 30, 45, 60, 90, 150, and 240 min from the beginning of the experiment. For temperatures above 50 °C, halve the intervals between the samples.

Transfer the samples (2 ml) from the reaction flask into the 100-ml beakers, each of which contained 10 ml of benzene and 20 ml of water cooled with ice for sharp lowering of the rate of exchange. Keep the beakers with the samples covered with watch glasses on ice for 5 min. Next transfer the mixture into the separatory funnels in which the layers separate after shaking. Take aliquot portions from each layer and put them into the test tubes for measuring the γ -activity of ^{131}I . Measure the activity of the samples in the test tubes in the course of work in the installation with the γ -radiation detector with an accuracy of $\pm 3\%$.

1. Plot the results of measurements on a graph of activity versus time and use it to appraise the degree of achievement of equilibrium.

2. Calculate the degree of exchange F for each point.

3. Plot $\log(1 - F)$ versus t .

4. Find the half-time of exchange $t_{1/2}$.

5. Determine the rate w of the exchange reaction for each point.

6. Assuming that $m + n = 2$, determine k — the rate constant of the exchange reaction for each point.

7. Averaging the values of k for each temperature, plot $\log k$ versus $1/T$.

8. Determine the activation energy E of the reaction from the plot and the value of pZ .

9. Indicate the absolute and relative errors of the obtained values.

Experiment 6.5. ISOTOPE EXCHANGE OF IODINE BETWEEN SOLUTION OF NaI AND SOLID AgI [8]

The isotope exchange of iodine between solid silver iodide and sodium iodide in a solution proceeds via the dissociation of both components. But the rate and degree of exchange depend on the state of the precipitate. The exchange of iodine between an aged silver iodide precipitate and the iodide ions proceeds slowly, and only from the surface because the diffusion of iodine into the crystal lattice of AgI goes on with difficulty.

Equipment and Reagents

Equipment and Utensils. A counting installation with a detector of γ -radiation. A centrifuge. Beakers for 100 ml (5). A funnel for filtration.

Radioactive Substances. A 0.05 M solution of NaI containing ^{131}I with a specific activity of 300 cpm/ml.

Reagents. Solutions: 0.1 M AgNO_3 ; 0.1 M NaI; 0.5 N HNO_3 .

Performance of Work

Pour 3 ml of a 0.1 M solution of AgNO_3 into each of four centrifuge tubes. Pour in an equivalent amount of a solution of inactive NaI. Centrifuge the precipitate, pour off the solution and wash the precipitate twice with water, then centrifuge it again.

Pour an active solution of NaI in an amount equivalent to the AgNO_3 into the first tube. Record the time of adding this solution. Rapidly bring it up to boiling and, after recording the time, cool it with iced water. Centrifuge the precipitate, pour off the solution into a beaker, and then wash the precipitate by decantation. Join the washing water to the basic solution and precipitate I^- from it with silver nitrate. After 30 min, separate the precipitate and measure its activity.

Simultaneously pour active NaI into the three remaining test tubes and rapidly bring the solution up to boiling. Record the time of adding the solution and stop the heating in 5, 15, and 30 min by placing the tubes into iced water. Next separate the precipitates by centrifuging and treat the filtrate as described above.

Next use silver nitrate to precipitate silver iodide from 6 ml of an active solution of NaI. Filter the precipitate off in 30 min. Measure its activity in the same way. Reduce the activity of all the precipitates to the same time. Calculate the degree of exchange for all the samples, having in view that in the given case the specific activity may be replaced with the total activity of the solution.

Plot $\log(1 - F)$ versus t .

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Part II The Chemistry of Nuclear Transformations

Chapter 7 Chemical Processes with the Participation of Hot Atoms [1]

THEORETICAL INTRODUCTION

The atoms of a radioactive isotope formed as a result of nuclear transformations in the majority of cases break their chemical bonds in the parent compound and form **recoil** or **hot** atoms. The latter enter into chemical reactions with surrounding molecules and form labelled substances, or are thermalized and remain (as a result of "cooling") in the free or ionic state. Using the ability of the recoil atoms to enter into such reactions, one can separate the free radioactive atoms from the initial parent compound, enrich isotopes or obtain them without a carrier, and also obtain labelled compounds.

A convenient model for studying the reactions of hot atoms is the performing of the processes ${}^h\text{X} (n, \gamma) {}^{h+1}\text{X}$ in liquid alkyl halides in the presence of various substances—elementary bromine as an acceptor of radicals and aniline as a substance entering into reactions with excited molecules of alkyl halides with $E_{\text{act}} \approx 42$ kJ/mol.

A quantitative measure of the reaction of recoil atoms is the **apparent' retention**—the ratio of the concentration of the labelled organic reaction products to the concentration of all the labelled products, both organic and inorganic. The retention—the yield of the labelled parent substance and the yield of a given product—is the ratio of the concentra-

tion of the relevant substance to that of all the products. By studying the dependence of the retention and the yield of separate products on the concentration of added substances, one can determine the contribution of high-energy and thermal reactions of recoil atoms, and also the fraction of labelled molecules which after the reaction of their formation enter into secondary reactions with other substances.

A mathematical description of processes with the participation of hot atoms is often based on the concept of the physics of the thermalization and capture of neutrons in a natural mixture of uranium isotopes. If the probability of avoiding the resonance capture of neutrons by the isotope ^{238}U in the process of their thermalization after the fission of ^{235}U is

$$\eta = \exp \left[-\frac{1}{\xi} \int_{E_1}^{E_2} \frac{\Sigma_c(E)}{\Sigma_c(E) + \Sigma_{sc}(E)} \frac{dE}{E} \right] \quad (7.1)$$

where ξ is the logarithmic decrement of the energy; $\Sigma_c(E)$ is the macro cross section of capture, and $\Sigma_{sc}(E)$ is the macro cross section of scattering, then $(1 - \eta)$ is the probability of a reaction. Provided that the recoil atoms are retarded according to a mechanism of elastic collisions and enter into chemical reactions within a sufficiently narrow energy interval, the integrand in formula (7.1) can be written in the form ε/ν , where ε is the energy of a liquid cell and ν is the energy of a chemical bond, and the reaction yield, in the form:

$$R = 1 - \eta = f \frac{\varepsilon}{\nu \xi} \ln \left(\frac{E_r}{\nu} \right) \quad (7.2)$$

where f is the probability of colliding with molecules of the given species, and E_r is the recoil energy. The following formula is used for comparison with experimental results:

$$R = \text{const} \left(\frac{f}{\xi} \right) \quad (7.3)$$

The probability of a collision is calculated by the formula

$$f_1 = \frac{N_1 \sigma_1}{N_1 \sigma_1 + N_2 \sigma_2} \quad (7.4)$$

where N_1 is the mole fraction of the mixture component, reaction with which is being studied, N_2 is the mole frac-

tion of the second component, σ_1 and σ_2 are the micro cross sections of collision with the first and second components of the mixture:

$$\sigma_1 = \pi (r_a + r_1)^2 \quad \sigma_2 = \pi (r_a + r_2)^2 \quad (7.5)$$

where r_a is the covalent radius of a recoil atom, r_1 and r_2 are the covalent radii of atoms of the first and second components of the medium with which the recoil atoms collide.

The logarithmic decrement of the energy for a mixture of substances can be calculated by the following relation:

$$\xi = \frac{N_1 \sigma_1 \xi_1 + N_2 \sigma_2 \xi_2}{N_1 \sigma_1 + N_2 \sigma_2} \quad (7.6)$$

where ξ_1 and ξ_2 are the logarithmic decrements of the energy for the first and second components of the mixture evaluated by the formula

$$\xi = 1 + \frac{1}{1-\alpha} \ln \alpha \quad (7.7)$$

Here

$$\alpha = \frac{(m-M)^2}{(m+M)^2}$$

where m is the mass of a recoil atom, and M is the mass of an atom in the molecule, a collision with which is being considered.

The reactions of recoil atoms in solid crystalline substances are often considered as proceeding in a "hot zone"—a region of a solid in which a high temperature develops when a recoil atom is retarded. Some reactions do not have time to proceed to the end during the time the zone exists, and therefore upon the following action of an elevated temperature the phenomenon of "annealing" is observed—a change in the retention and yield of separate products with time upon the isothermal ageing of specimens occurring as a result of reactions of metastable fragments.

Experiment 7.1. RETENTION AND SECONDARY REACTIONS OF HALOGEN RECOIL ATOMS IN ORGANIC COMPOUNDS [1, 2]

Owing to their recoil energy after an (n, γ) reaction, the newly formed atoms of the radioactive isotopes leave the parent molecules of organic compounds. The recoil atoms

upon thermalization partly enter into chemical reactions and partly are "cooled" to thermal speeds and can be separated by extraction with an aqueous solution of a carrier. The apparent retention is determined by the method of extraction. The yields of the separate labelled products can be determined upon the distillation of the organic fraction with added carriers.

The experiment consists in determining the fraction of the recoil atoms of halogens stabilized in the form of organic compounds, and the yields of separate labelled compounds formed after an (n, γ) reaction in alkyl halides.

A. REACTION $^{37}\text{Cl}(n, \gamma)^{38}\text{Cl}$ IN CCl_4

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of γ -radiation (a monocrystal of NaI with a well). A source of neutrons with an integral intensity of 10^7 - 10^8 cps. A paraffin block (at the centre of the block there is a cell for the source of neutrons, and at a distance of 5-6 cm from it there are cells for test tubes). An arrangement for distilling off CCl_4 . Test tubes for irradiation for 15 ml with ground-glass stoppers (glass of Grade BD-4). A separatory funnel for 100 ml. Conical flasks for 100 ml (2). Cupped counting planchets with ground-glass stoppers for 5 ml. A graduated cylinder for 30 ml. A device for sampling liquids for 5 ml (a pipette connected to a syringe by a rubber tube).

Reagents. Carbon tetrachloride. Bromobenzene. A solution of Na_2SO_3 (5%) containing a small amount of NaCl as a carrier.

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons.

Put the test tubes with CCl_4 (3, each containing 10 ml of CCl_4) into the paraffin block and irradiate them with neutrons for several hours. Shake the carbon tetrachloride (30 ml) irradiated by neutrons in the separatory funnel with 10 ml of the solution of $\text{Na}_2\text{SO}_3 + \text{NaCl}$, and then with 15 ml of water. Combine the inorganic extracts. Transfer 3 ml each of the organic and inorganic fractions into the counting planchets (separately), and then place the latter into the monocrystal well of the scintillation counter. Determine the apparent retention by measuring the activity of the organic and inorganic fractions.

Add 10 ml of a high-boiling carrier (bromobenzene) to 20 ml of the organic fraction and distil off the carbon tetrachloride, gathering 3 ml of the product into a counting planchet. Determine the yield of labelled carbon tetrachloride (the ratio of its activity to the total activity of the ^{38}Cl). Perform the work within 25-30 min with a view to the short half-life of ^{38}Cl . Reduce the measured activities to the same time.

B. REACTION $^{81}\text{Br}(n, \gamma)^{82m}\text{Br} \longrightarrow ^{82}\text{Br}$ IN CHBr_3

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of γ -radiation (a monocrystal of NaI with a well). A source of neutrons with an integral intensity of 10^7 - 10^8 cps. A paraffin block (at the centre of the block there is a cell for the source of neutrons, and at a distance of 5-6 cm from it there are cells for test tubes). An arrangement for vacuum distillation. Test tubes (3) for irradiation for 15 ml with ground-glass stoppers (glass of Grade BD-4). Burettes for 25 ml. A separatory funnel. Conical flasks for 100 ml. Beakers for 100 ml. Counting planchets. A vacuum desiccator.

Reagents. Bromoform. Carbon tetrachloride. Ethanol. Bromine. A solution of Na_2SO_3 (5%) containing a small amount of NaBr as a carrier. Carbon tetrabromide.

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons.

Irradiate the bromoform containing 10^{-3} mol of Br_2 with neutrons during 3-4 days. Shake the portion of irradiated bromoform (30 ml) in a separatory funnel with 10 ml of a solution of $\text{Na}_2\text{SO}_3 + \text{NaBr}$, and then with 15 ml of water. Combine the inorganic extracts. Transfer separately 3 ml each of the organic and inorganic fractions into the counting planchets. Place the latter into the monocrystal well of the scintillation counter and measure the activity. Add 5 g of CBr_4 to the organic fraction and distil off the bromoform at a reduced pressure until the residue in the flask solidifies ($t < 70^\circ\text{C}$). Place an aliquot part of the middle fraction of the distilled bromoform into a counting planchet. Dissolve the residue in 10-15 ml of ethanol, and then with the slow addition of water (dropwise) separate the CBr_4 . An amount of water is needed for this operation that equals half the

amount of ethanol used to dissolve the residue after distilling off the bromoform. Dry the separated CBr_4 in the vacuum desiccator. Transfer a weighed amount of the CBr_4 (0.5-0.8 g) into a counting planchet and add ethanol (to a total volume of 3 ml). Measure the activity of the bromoform and the CBr_4 . Determine the retention and the yields of the separate products of the reactions of the recoil bromine atoms with bromoform.

Experiment 7.2. HIGH-ENERGY AND DIFFUSION-RECOMBINATION (THERMAL) PROCESSES ATTENDING THE STABILIZATION OF HOT ATOMS [2]

The reactions of recoil atoms are divided into high-energy processes not depending on the temperature and the presence of radical acceptors and only slightly depending on the phase state of the medium, and diffusion-recombination reactions depending on the factors listed above. The retention and the yields of reactions of hot bromine atoms in the presence of bromine as a radical acceptor are determined in the experiment.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of γ -radiation (a monocrystal of NaI with a well). A source of neutrons with an integral intensity of 10^7 - 10^8 cps. A paraffin block (there is a cell for the source of neutrons at the centre of the block; at a distance of 5-6 cm from it there are cells for test tubes made from Grade BD-4 glass). Instead of the test tubes, one may use a 0.5-litre flask with the source of neutrons placed at its centre. The flask is placed in the paraffin block. An arrangement for vacuum distillation. A distillation column (8-10 theoretical plates). Cupped counting planchets for 5 ml (4). Test tubes for irradiation for 30 ml (10). Conical flasks for 100 ml (2).

Reagents. Dibromoethane. Bromoform. Bromine. Na_2SO_3 (crystalline). CaCl_2 (calcined).

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons.

Irradiate methylene bromide (30 ml) containing elementary bromine in an amount of 10^{-3} , 0.01, 0.05, 0.1, 0.15, 0.2, and 0.3 mol with neutrons during four days. Do this in test tubes with ground-glass stoppers placed in the paraffin

block. Put 30 ml of the irradiated methylene bromide and 50 ml of water in a separatory funnel and, by adding crystalline Na_2SO_3 in small portions, shake them until the colour of bromine vanishes. Separate the organic and inorganic fractions. Wash the organic fraction with water (10 ml). Combine the inorganic extracts. Put 3 ml of each fraction into the counting planchets. Add 20 ml of CHBr_3 and several pieces of the calcined CaCl_2 for absorbing water to 20 ml of the organic fraction. Distil the mixture. First distil off the methylene bromide in the column, and then the bromoform under a vacuum. Determine the activity of the fraction CH_2Br_2 and CHBr_3 (3 ml each). Find the yields of $\text{CH}_2\text{Br}^{82}\text{Br}$ and $\text{CHBr}_2^{82}\text{Br}$ depending on the concentration of the added bromine—the acceptor of the hot bromine atoms.

Calculate the probability f of collision of the recoil atoms of ^{82}Br with the bromine atoms in the CH_2Br_2 , and also the logarithmic decrement ξ of the energy in retardation of the recoil atoms in a medium of $\text{CH}_2\text{Br}_2 + \text{Br}_2$. Plot the yield of the labelled parent compound versus f/ξ and check the correctness of formula (7.3). Show the presence of two processes: high-energy reactions not depending on the additions of an acceptor of radicals, and diffusion-recombination (thermal) reactions inhibited by small amounts of the acceptor. Explain the formation of $\text{CHBr}_2^{82}\text{Br}$.

Experiment 7.3. ROLE OF EXCITED MOLECULES IN REACTIONS OF RECOIL ATOMS [3]

The molecules appearing in reactions of hot bromine atoms with alkyl bromides are excited. The excitation energy is sufficient for such molecules to be able to enter into a reaction with aniline. As a result of this reaction, the radioactive isotope is in an easily separated chemical form, and according to the diminishing radioactivity of the organic fraction (or to the increasing activity of the inorganic fraction) one can appraise the fraction of molecules excited as a result of reactions with the participation of hot atoms.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of γ -radiation (a monocrystal of NaI with a well). A source of neutrons with an integral intensity of 10^7 - 10^8 cps. A paraffin block (there is

a cell for the source of neutrons at the centre of the block; at a distance of 5-6 cm from it there are cells for test tubes). An arrangement for distillation under a vacuum. A distillation column (8-10 theoretical plates). Test tubes for irradiation for 30 ml (10). Cupped counting planchets for 5 ml (4). Measuring flasks for 50 ml (2).

Reagents. Aniline (freshly distilled). A solution of NaBr (0.1 M). HCl (concentrated acid diluted in the proportion of 1 : 1). CH_2Br_2 .

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons.

Irradiate the mixture of methylene bromide with aniline as described in Experiment 7.2.

Treat the irradiated methylene bromide (30 ml) containing aniline (0.01, 0.03, 0.06, 0.1, 0.15, 0.2, 0.3, 0.5, 0.7 mol) in a separatory funnel four times with portions of 10 ml of a 0.1 N solution of NaBr. Wash off the organic fraction with the HCl solution (1 : 1) up to complete removal of the aniline, and then wash it with water. Collect the hydrochloric acid and water extracts separately in 50-ml measuring flasks.

Measure the activity of aliquot parts (3 ml each) of the organic and hydrochloric acid extracts. Distill off the methylene bromide in the column after drying it over CaCl_2 and measure its activity.

Plot the yield of $\text{CH}_2\text{Br}^{82}\text{Br}$ against the mole fraction of aniline. Compare the results obtained with data on the yield of $\text{CH}_2\text{Br}^{82}\text{Br}$ in the mixture $\text{CH}_2\text{Br}_2 + \text{Br}_2$ (see Experiment 7.2).

Experiment 7.4. CHECKING THE THEORY OF ELASTIC COLLISIONS ON THE EXAMPLE OF THE REACTIONS OF RECOIL BROMINE ATOMS IN BINARY SYSTEMS [4]

If processes with the participation of hot atoms obey the laws that hold provided that kinetic energy is transferred in elastic collisions, the yield of a labelled parent compound should be determined by the probability of a collision and the logarithmic decrement of energy [formula (7.3)].

The object of the present experiment is to study the chemical consequences of the reaction $^{81}\text{Br}(n, \gamma)^{82m}\text{Br} \rightarrow ^{82}\text{Br}$ in the system $\text{C}_2\text{H}_5\text{Br} + \text{CCl}_4$ in order to verify formula (7.3).

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of γ -radiation (a monocrystal of NaI with a well). A source of neutrons with an integral intensity of 10^7 - 10^8 cps. A flask for irradiation (the neutron source is placed at the centre of the flask, and the latter is placed in a paraffin block). A distillation column (10 theoretical plates). Cupped counting planchets for 5 ml. Conical flasks for 100 ml. A separatory funnel.

Reagents. Ethyl bromide. Carbon tetrachloride. A solution of Na_2SO_3 (5%) containing a small amount of NaBr as a carrier.

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons.

Irradiate the ethyl bromide containing 0, 0.3, 0.5, 0.7, and 0.9 mol of CCl_4 with neutrons during three or four days. Treat the irradiated mixtures in the separatory funnel with 30 ml of a solution of $\text{NaBr} + \text{Na}_2\text{SO}_3$, and then with 20 ml of water. Take an amount of a mixture each time that contains 25 ml of ethyl bromide. Put 3 ml each of the organic and inorganic fractions in the counting planchets. Distil the remaining organic fraction in the distillation column, collecting 3 ml of ethyl bromide in each of five planchets. Determine the activity of the organic, inorganic, and ethyl bromide fractions. Calculate the retention and yield of the $\text{C}_2\text{H}_5^{82}\text{Br}$ at various concentrations of the CCl_4 in the initial mixture (take the radioactivity of the middle fraction for calculation). Evaluate the ratio f_1/ξ [see formula (7.3)]. Plot the yield of $\text{C}_2\text{H}_5^{82}\text{Br}$ versus the ratio f_1/ξ . Arrive at a conclusion on the mechanism of reactions with the participation of hot recoil atoms of ^{82}Br in the given system.

Experiment 7.5. CHEMICAL BEHAVIOUR OF HOT BROMINE ATOMS IN SOLID KBrO_3 [5]

The chemical effects produced by hot atoms in solid crystalline inorganic substances differ from the processes occurring in organic substances. The presence of a crystal lattice does not allow the hot atoms to enter into rapid recombination reactions with the fragments formed in thermalization. Heating is attended by reactions that do not have time to proceed to the end during the time of existence of the hot zone—"annealing" processes.

The experiment is aimed at studying the behaviour of recoil atoms of ^{82}Br formed according to the reaction $^{81}\text{Br}(n, \gamma)^{82m}\text{Br} \rightarrow ^{82}\text{Br}$ in solid crystalline potassium bromate.

Equipment and Reagents

Equipment and Utensils. A counter with a scintillation detector of γ -radiation. A source of neutrons with an integral intensity of 10^7 - 10^8 cps. A paraffin block (there is a cell for the source of neutrons at the centre of the block; at a distance of 5-6 cm from it there are cells for the test tubes with the substance to be irradiated). A drying cupboard (180°C). An analytical balance. Measuring flasks for 50 ml (6); the measuring flasks are counting planchets. A test tube with a ground-glass stopper.

Reagents. Freshly recrystallized KBrO_3 . Bromine water. Carbon tetrachloride.

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons.

Irradiate 25 g of KBrO_3 with neutrons during three days. Dissolve the irradiated salt (1.5 g) in bromine water in a 50-ml measuring flask and measure the total activity of the sample. To do this, place the measuring flask over the crystal of the scintillation counter. Transfer the content of the flask into a separatory funnel and extract the bromine with carbon tetrachloride (twice with 25 ml each time). Combine the organic extracts and measure their activity in a 50-ml measuring flask. In this way, the yield of ^{82}Br in the form of Br^- and Br^0 is determined. Find the activity of the ^{82}Br in the form of BrO_3^- according to the difference between the total activity and the activity of the ^{82}Br in the form of Br^- and Br^0 . Put the remaining amount of salt in the drying cupboard (in the test tube with the ground-glass stopper) and anneal it at 180°C , periodically determining the activity of the ^{82}Br in the form of the bromate. To do this, in 1, 2, 3, 5, and 25 hours take 1.5 g of KBrO_3 from the tube, dissolve the sample in bromine water, and extract the bromine with carbon tetrachloride as described above. Use the measured activities to find how the yield of ^{82}Br in the form of the bromate depends on the duration of annealing.

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Chapter 8 Methods of Preparing and Separating Artificial Radioactive Isotopes [1-3]

THEORETICAL INTRODUCTION

At present, radioactive isotopes of almost all the elements of D. Mendeleev's Periodic Table can be prepared. The nuclear reactions used for this purpose occur under the action of slow and fast neutrons, deuterons, protons, α -particles, and the electromagnetic radiation of a betatron (quanta of very hard radiation). Some radioactive isotopes can be separated from the fission products of uranium or other heavy elements (the processing of nuclear fuel).

The radioactive isotopes are separated from the target in various ways (by means of extraction, chromatography, coprecipitation with an isotope, isomorphic or inert carrier, distillation, leaching out, electrolysis, adsorption, etc.).

A. NEUTRON-INDUCED NUCLEAR REACTIONS

Fast neutrons (neutrons with a high energy) produce what we call threshold reactions: (n, p) , (n, α) , $(n, 2n)$, etc. When the reactions (n, p) and (n, α) are used, radioactive isotopes are produced without a carrier.

When fast neutrons pass through a substance, their inelastic scattering occurs in addition to nuclear reactions. As a result of the scattering, the energy of the neutrons

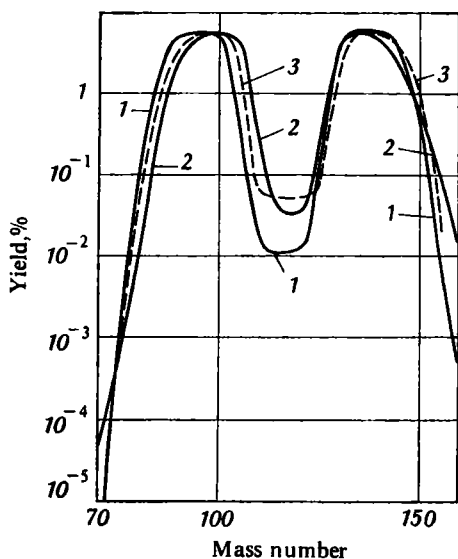


Fig. 8.1. Yield of fission products of ^{235}U (1), ^{239}Pu (2), and ^{238}U (3)

diminishes. Substances containing elements with a small atomic number such as hydrogen, deuterium, and carbon are customarily used as neutron moderators. These substances may include, for example, water, paraffin, and graphite. Slow (thermal) neutrons are in thermal equilibrium with the surroundings, and at 25°C their mean energy is 0.025 eV, and their mean speed is 22 m/s.

The reaction (n, γ) mainly occurs when targets are irradiated with slow neutrons. The reactions (n, p) and (n, α) also occur under the action of slow neutrons only with light elements. Neutrons also cause fission reactions (n, f) of heavy nuclei, for example ^{235}U , ^{239}Pu , etc. In fission, radioactive isotopes of the periodic table with atomic numbers from 30 to 63 (from zinc to europium) form. Figure 8.1 shows curves of the distribution of uranium and plutonium fission products by masses.

The most convenient source of fast and slow neutrons is a reactor, in which they are obtained upon the fission of uranium or plutonium. The maximum energy of uranium

fission neutrons is 14 MeV. The density of the neutron flux in nuclear reactors is 10^{14} - 10^{19} neutron/(m²·s). It is convenient to obtain fast neutrons in cyclotrons and linear accelerators using the following nuclear reactions: ${}^7\text{Li}(d, n){}^8\text{Be}$; ${}^9\text{Be}(d, n){}^{10}\text{B}$; ${}^2\text{H}(d, n){}^3\text{He}$.

Lately neutron generators have been introduced quite successfully. The neutrons are produced in them by the reaction ${}^2\text{H}({}^3\text{H}, n){}^4\text{He}$. In these generators, the deuterium ions are accelerated to an energy of 100-200 keV and bombard titanium or zirconium targets saturated with tritium. Neutron generators make it possible to obtain a neutron flux density of the order of 10^9 - 10^{14} neutron/(m²·s) and a neutron energy of the order of 14 MeV.

In laboratory conditions, the reactions (α, n) and (γ, n) are used to obtain a flux of neutrons. Most often the sources ${}^{226}\text{Ra}$ -Be, ${}^{210}\text{Po}$ -Be, ${}^{239}\text{Pu}$ -Be, and ${}^{124}\text{Sb}$ -Be are used, as well as sources emitting spontaneous fission neutrons from ${}^{252}\text{Cf}$. The neutron flux of the laboratory sources of neutrons is 10^5 - 10^8 neutron/s.

The yield of a radioactive isotope upon the irradiation of a target with fast or slow neutrons, deuterons, protons, or other particles is evaluated by the formula

$$A = \lambda N' = F_0 k s (1 - e^{-\sigma L}) (1 - e^{-\lambda t}) \quad (8.1)$$

where A is the absolute activity (yield) of the radioactive isotope obtained, dps*, λ is the radioactive decay constant of the isotope, s⁻¹, N' is the number of atoms of the radioactive isotope, F_0 is the flux density of the nuclear particles (neutrons, deuterons, protons, α -particles, γ -quanta), cps/m², k is a coefficient taking into account the loss of nuclear particles as a result of secondary processes (other nuclear reactions, scattering, etc.); if no secondary nuclear reactions occur, then $k = 1$, s is the surface area of the target, m², σ is the cross section of activation of the given nuclear reaction reduced to a natural mixture of isotopes, m²/atom**,

* The yield is often given in other units in the literature, for example, kBq/($\mu\text{A} \cdot \text{h}$) [$\mu\text{Ci}/(\mu\text{A} \cdot \text{h})$].

** The term "activation cross section" is most frequently a synonym of the term "effective cross section" or simply "cross section" of a given nuclear reaction. The section of nuclear reactions is expressed in m²/atom or in barns (1 barn = 10^{-24} cm²/atom).

L is the concentration of atoms on which the given nuclear reaction proceeds, atom/m³, l is the thickness of the target, m, and t is the duration of irradiating the target with nuclear particles, s.

The value of L is calculated by the formula

$$L = \frac{m\varepsilon \times 6.02 \times 10^{23}}{A_m}$$

where m is the mass of 1 m³ of the target, g, ε is the fraction of the element in the target on whose nuclei the given nuclear reaction proceeds, and A_m is the mass of one mole of the element.

Formula (8.1) holds if we may disregard the decrease in the concentration of an element during irradiation of the target. For a spherical target with the source of nuclear particles at its centre, by the thickness of the target in formula (8.1) is meant the difference between the radii r of the target and r_0 of the source, i.e. $l = r - r_0$. In this case instead of the quantity $F_0 \cdot s$ in formula (8.1), we use the quantity F_s —the flux of particles through the entire angle 4π (in cps).

If the activation cross section of a given nuclear reaction is not very large and the decrease in the particle flux inside the target may be disregarded, the exponential in the first parentheses of formula (8.1) may be expanded into a series. Using only the first two terms of the expansion, we obtain

$$A = \lambda N' = F_0 k s l L \sigma (1 - e^{-\lambda t}) = F_0 k \sigma N (1 - e^{-\lambda t}) \quad (8.2)$$

where $N = Lls$ is the number of atoms of the element in the target on which the given nuclear reaction proceeds and a radioactive isotope is obtained.

Formula (8.2) also holds for evaluating the yields of radioactive isotopes obtained by the reaction (n, γ). Here the density of the neutron flux is

$$F_0 = n_v \bar{v}_n$$

where n_v is the concentration of the neutrons at a given point of space, neutron/m³, and v_n is the mean speed of the neutrons, m/s.

In evaluating the yields of radioactive isotopes by for-

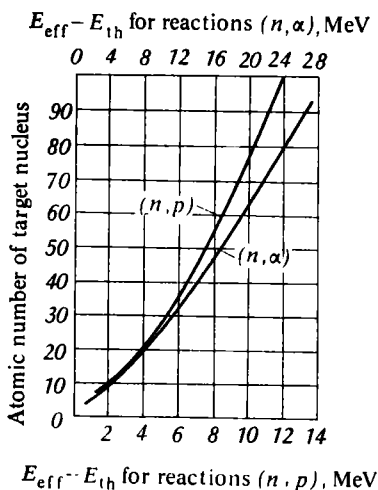


Fig. 8.2. Dependence of $E_{\text{eff}} - E_{\text{th}}$ on atomic number of target nucleus for reactions (n, p) and (n, α)

mulas (8.1) and (8.2), one must know the flux density or flux of particles (F_0 or F_s), the value of k , and the cross section of the nuclear reaction. The values of F_0 or F_s are usually known for a given source of nuclear particles, while the activation cross section of a nuclear reaction produced by neutrons is taken from the published data. Appendices 8 and 10 give the values of the activation cross section of the nuclear reaction (n, γ) produced by slow neutrons, and the reactions (n, p) and (n, α) produced by fission neutrons in a heterogeneous graphite-uranium reactor. If the cross section of the desired reaction (n, p) or (n, α) is absent in the table given in the Appendix, the semiempirical method proposed by D. Hughes may be employed. Let us consider as an example of employing Hughes's method the finding of the activation cross section of the reaction $^{59}\text{Co}(n, p)^{59}\text{Fe}$ caused by fission neutrons. We first calculate the heat effect of the nuclear reaction Q , which in atomic mass units* (amu) equals the sum of the differences between

* 1 amu corresponds to 931.7 MeV.

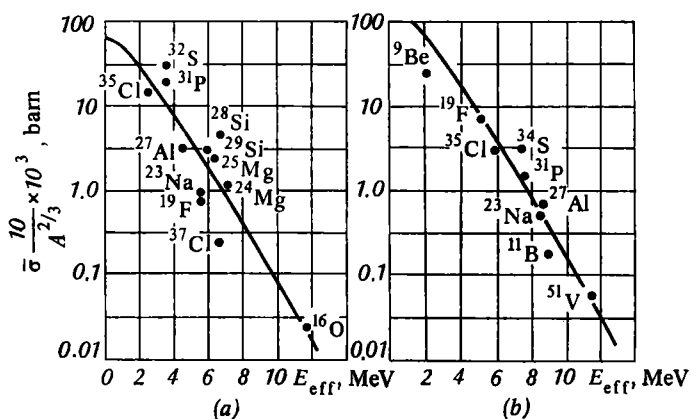


Fig. 8.3. Averaged effective cross sections:
a—reactions (n, p); b—reactions (n, α)

the masses of ^{59}Fe and ^{59}Co and between a neutron and a proton (see Appendix 3):

$$\begin{aligned}
 Q &= (M_{^{59}\text{Fe}} - M_{^{59}\text{Co}} + M_n - M_p) \\
 &= -(58.953\,615 - 58.951\,940 + 1.008\,986 \\
 &\quad - 1.008\,145) = -0.000\,834 \text{ amu} \\
 &= 0.000\,834 \times 931.7 = -0.78 \text{ MeV}
 \end{aligned}$$

Next we calculate the threshold of the given reaction E_{th} :

$$E_{\text{th}} = Q \frac{M_{^{59}\text{Fe}} + 1}{M_{^{59}\text{Fe}}} = -0.78 \times \frac{60}{59} = -0.79 \text{ MeV}$$

Now, using Hughes's method, we find in Fig. 8.2 the effective surplus of energy above the reaction threshold: $E_{\text{eff}} - E_{\text{th}} = 4.3 \text{ MeV}$, whence $E_{\text{eff}} = 4.3 + 0.79 = 5.2 \text{ MeV}$. Using the found value of E_{eff} , in Fig. 8.3 we determine the mean effective cross section of activation of the given nuclear reaction $\bar{\sigma}$ multiplied by the factor $1/(M_{^{59}\text{Co}})^{2/3}$.

$$\bar{\sigma} \frac{10}{(M_{^{59}\text{Co}})^{2/3}} = 2 \times 10^{-3} \text{ barn}$$

And, finally, we find the value of $\bar{\sigma}$:

$$\begin{aligned}\bar{\sigma} &= 2 \times 10^{-3} \frac{(M_{59\text{Co}})^{2/3}}{10} = 2 \times 10^{-3} \frac{(59)^{2/3}}{10} \frac{2 \times 10^{-3} \times 11.5}{10} \\ &= 2.3 \times 10^{-3} \text{ barn} = 2.3 \text{ mbarn}\end{aligned}$$

In the SI, we have $\bar{\sigma} = 2.3 \times 10^{-31} \text{ m}^2/\text{atom}$.

The evaluated activation cross section coincides quite well with the experimentally obtained value.

B. NUCLEAR REACTIONS INDUCED BY CHARGED PARTICLES (PROTONS, DEUTERONS, α -PARTICLES)

All reactions induced by charged particles are threshold ones.

If a radioactive isotope is produced by irradiating a target with particles obtained in an accelerator (cyclotron, synchrotron, etc.), and the target has a thickness much smaller than the path of the particles in the irradiated substance, formulas (8.1) and (8.2) may be used to evaluate the yield of the radioactive isotope. If, on the other hand, the target has a thickness at which the particles are absorbed completely, the activity of the irradiated target is calculated by the formula

$$A = BF_s k (1 - e^{-\lambda t}) \quad (8.3)$$

where B is the activity of the formed isotope when one particle strikes the target (the target is made from an individual substance and its thickness is larger than the path of particles having a given energy), F_s is the flux of particles from the source (in the given case all the particles strike the target), cps, and k is a coefficient taking into account the fraction of the particle flux participating in the formation of the isotope of interest to us (for an individual substance, $k = 1$).

For deuterons or other singly charged particles, we have:

$$A = 6.3 \times 10^{12} i B k (1 - e^{-\lambda t}) \quad (8.4)$$

where i is the current, μA , and 6.3×10^{12} is a coefficient equal to the number of particles striking the target a second at an ionic current in the cyclotron equal to 1 μA .

If the duration of irradiation is small, $e^{-\lambda t}$ may be expanded into a series, and formula (8.3) acquires the form:

$$A = BF_g k \lambda t \quad (8.5)$$

The yields of radioactive isotopes A_i [in kBq/($\mu\text{A} \cdot h$) or in $\mu\text{Ci}/(\mu\text{A} \cdot h)$] that have been determined experimentally when irradiating a thick target with particles during a time much shorter than the half-life are usually tabulated (see Appendix 9). Using these values, we can evaluate the yield of a radioactive isotope by the following formula:

$$A = 3.7 \times 10^4 A_i t i \quad (8.6)$$

where A is the absolute activity (yield), dps, t is the duration of irradiation, h, and i is the current in the accelerator, μA .

A comparison of formulas (8.5) and (8.6) reveals that $F_g B k \lambda = 3.7 \times 10^4 A_i$.

Experiment 8.1. DETERMINING THE RELATIVE CROSS SECTION OF NUCLEAR REACTIONS [1, 4]

It is sometimes necessary to know the relative cross sections of nuclear reactions. If targets containing an identical number of atoms of various elements are irradiated by nuclear particles in identical conditions, then by formulas (8.1) and (8.2) the activities of the radioactive isotopes obtained are proportional to the cross sections of the relevant nuclear reactions.

The present experiment is aimed at determining the relative cross section of the reactions (n, γ) in the irradiation of manganese, copper, silver, gold, and zinc.

Equipment and Reagents

Equipment. A counter for registering β -radiation. A laboratory source of neutrons ($F_g \geq 10^6$ neutron/s). A paraffin block for irradiation.

Materials. Plates made from copper, manganese, silver, gold, and zinc (the thickness of the plates expressed in terms of the number of atoms per m^2 must be the same).

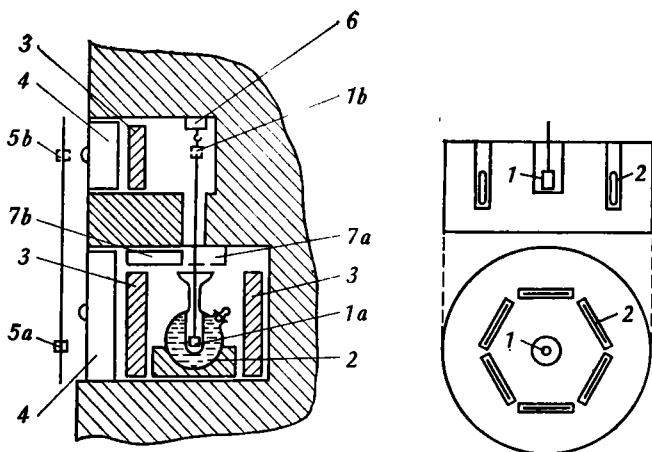


Fig. 8.4. Arrangement for irradiating targets with neutrons in a laboratory:

1—radium- or polonium-beryllium source (position *b* when installing or extracting the target, position *a* when irradiating the target); 2—flask with liquid target; 3—paraffin neutron moderator; 4—doors of safes; 5—indicator of neutron source position (*a*—source is in tube inside target; *b*—source is in upper safe; 6—motor lifting and lowering neutron source; 7—door of upper safe (position *a* when irradiating the target, position *b* when installing or extracting the target)

Fig. 8.5. Paraffin block for irradiating metal plates:
1—neutron source; 2—metal plates (targets)

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons.

Figure 8.4 shows an arrangement that can be used for irradiating targets with neutrons in a laboratory.

Plates made from copper, manganese, silver, gold, cobalt, and zinc are irradiated with slow neutrons during a time such that the integral flux of neutrons $F_0 t$ will be 2×10^{10} – 10^{11} . For this purpose, put plates of the same area and thickness (in atom/m²) into the grooves of a paraffin block (Fig. 8.5). Accurately measure the duration of irradiation of each plate. Extract the plates in turn with pincers, registering the time of removal from irradiation; measure their activity from five to seven times during a period equal to one-fourth half-lives; plot the results obtained in coordinates of the logarithm of the activity against the time, and by extrapolating

the data find the activity of each plate at the instant of termination of irradiation.

Since self-absorption of β -particles occurs in the layer of irradiated material, the relevant correction must be introduced. For this purpose, use the law of self-absorption of β -particles and tabulated values of the absorption coefficients. Take into account the absorption of the β -particles by the layer of air and the walls of the counter. After introducing all the above corrections into the measured rate of counting, we obtain I_{cor} :

$$I_{\text{cor}} = \nu_{\text{form}} \eta (1 - e^{-\lambda t})$$

where ν_{form} is the rate of formation of the radioactive isotope, η is the geometric coefficient of the counter, and t is the duration of irradiation with neutrons.

The quantity $\nu_{\text{form}} \eta$ is proportional to the reaction cross section. Adopting the cross section of formation of ^{56}Mn as unity, find the relative cross sections of the other nuclear reactions. Knowing that the magnitude of the activation cross section of the reaction $^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$ is $10.7 \times 10^{-28} \text{ m}^2/\text{atom}$ (10.7 barn), find the absolute values of the activation cross sections for the other nuclear reactions. Compare the results obtained with the published data.

Experiment 8.2. YIELD OF ^{108}Ag [1, 3]

When silver is irradiated with slow neutrons, its radioactive isotopes ^{108}Ag , ^{110}Ag , and ^{110m}Ag are obtained. The half-life of ^{108}Ag is 2.3 min, of ^{110m}Ag is 253 days, and of ^{110}Ag is 24.5 s. Upon a short duration of target irradiation, ^{108}Ag is mainly produced. When measuring the activity of ^{108}Ag , an appreciable decay of this isotope occurs, which must be taken into consideration in determining the yield of ^{108}Ag . In the given case, it is more convenient to measure the number of decayed ^{108}Ag atoms during a noticeable period of time.

The yield of ^{108}Ag can be calculated by the formula

$$W = \frac{\Delta I A_m}{\varphi e^{-\lambda t_2} (1 - e^{-\lambda t_3}) 6.02 \times 10^{23}} \quad (8.7)$$

where W is the yield of ^{108}Ag , g, ΔI is the number of registered counts during the time of measuring t_3 , A_m is the atomic

mass of Ag, ϕ is the counting coefficient, λ is the decay constant of ^{108}Ag , and t_2 is the time elapsed from the instant of removing the Ag from irradiation to the instant of beginning the radioactivity measurement.

The neutron flux density F_0 is determined by the formula:

$$F_0 = \frac{\Delta I \lambda A_m}{\phi m \times 6.02 \times 10^{23} \sigma e^{-\lambda t_2} (1 - e^{-\lambda t_3}) (1 - e^{-\lambda t_1})} \quad (8.8)$$

where m is the mass of the metallic silver, $m = sl\rho$, g , s is the area of the plate, m^2 , l is its thickness, m , ρ is the density of metallic silver, g/m^3 , t_1 is the duration of irradiating the target with neutrons.

Equipment and Reagents

Equipment. A laboratory source of neutrons (10^6 - 10^7 cps). A counter with a detector of β -particles. A paraffin block (see Fig. 8.5).

Materials. Silver foil with a thickness of $l = 3 \times 10^{-4}$ m and an area of $s = 2.5 \times 10^{-3}$ m^2 . An aluminium substrate.

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons.

Irradiate the silver foil with a mass of ~ 50 mg placed on the aluminium substrate for 10 min (t_1) with slow neutrons from the laboratory source in the paraffin block.

After the strictly definite time t_2 elapses needed for decay of the short-lived silver radioactive isotope ^{110}Ag (not over 3 min), use the counter with the detector of β -radiation to determine the total number of disintegrations ΔI in the irradiated foil during the definite time t_3 (4-6 min).

Determine the counting coefficient ϕ beforehand, or it must be known.

The effective cross section of the nuclear reaction produced by slow neutrons is 44.5 barn for the isotope ^{107}Ag .

Use the values of ΔI , t_1 , t_2 , and t_3 to calculate the yield of the radioactive atoms ^{108}Ag and determine the neutron flux density F_0 [see formulas (8.7) and (8.8)].

Experiment 8.3. DETERMINING THE CROSS SECTION OF A NUCLEAR REACTION ACCORDING TO THE YIELD OF THE RADIOACTIVE ISOTOPE [1, 3]

To determine the absolute value of the cross section of a nuclear reaction, one must know the amount of the radioactive isotope obtained during the given time interval when a known flux of nuclear particles passes through a known amount of substance [see formulas (8.1) and (8.2)].

The present experiment is aimed at determining the cross section of the reaction $^{35}\text{Cl}(n, \alpha)^{32}\text{P}$ produced by neutrons from a laboratory source.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A source of neutrons ($F_s = 10^6$ - 10^7 neutron/s). A round-bottom flask for irradiation with a diameter of 0.10-0.15 m (see Fig. 8.4). An arrangement for distilling off liquids (carbon tetrachloride).

Reagents. Carbon tetrachloride.

Performance of Work

Before beginning the experiment, acquaint yourself without fail (1) with the rules for working with a source of neutrons (see Fig. 8.4).

Determine the radius r of the flask for irradiation and the radius r_0 of the place in the tube soldered from below containing the neutron source.

Fill the flask with CCl_4 . Next place the neutron source into the flask and irradiate it during a time such that the integral flux of neutrons ($F_s t$) will be 5×10^{10} - 10^{11} . Record the time of beginning and terminating irradiation. Extract the radioactive phosphorus produced by the reaction $^{35}\text{Cl}(n, \alpha)^{32}\text{P}$ from the target following the procedure set out in Experiment 8.5 (Sec. B). Measure the activity of the obtained ammonium phosphomolybdate or magnesium ammonium phosphate in a counter for which the geometric coefficient is known. Introduce all the required corrections into the result obtained in measuring the activity and determine the activity of the ^{32}P in the preparation (in dps). Evaluate the cross section of the nuclear reaction $^{35}\text{Cl}(n, \alpha)^{32}\text{P}$ averaged over the entire spectrum of neutron energies from the given source [see formula (8.1)]. Compare the result obtained with published data.

Experiment 8.4. DIFFERENCE IN ACTION OF FAST AND SLOW NEUTRONS [1, 3]

Reactions (n, γ) are performed by irradiating targets with slow neutrons, whereas threshold reactions (n, p) and (n, α) are produced, as a rule, by fast neutrons. The object of the present experiment is to consider the difference in the action of fast and slow neutrons.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of β -radiation. A laboratory neutron source ($F_s = 10^6$ - 10^7 neutron/s). A paraffin block $0.1 \times 0.1 \times 0.05$ m.]

Materials. A silver or rhodium plate $0.06 \times 0.05 \times 0.001$ m in size.

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons (see Fig. 8.4).

Put the silver (rhodium) plate at a distance of 0.05 m from the neutron source and irradiate it for 10 min. (The integral flux of neutrons should be about 10^9 .) After terminating irradiation of the plate, measure its activity not later than in 2-5 min after irradiation. Next obtain the data needed for the decay curve. Repeat the experiment in the same conditions, but place a layer of paraffin 0.05 m thick between the plate and the neutron source. Measure the activity of both preparations in the counter with the detector of β -radiation and compare the obtained values. Arrive at a conclusion on how the neutron moderator affects the yield of radioactive isotopes of silver or rhodium.

Explain the results obtained.

Experiment 8.5. PREPARATION OF RADIOACTIVE ISOTOPES BY IRRADIATION WITH NEUTRONS [1, 4, 5]

This experiment can be performed with a laboratory source of neutrons and in a nuclear reactor.

A. PREPARATION OF ^{24}Na

Radioactive sodium₄ is prepared by the reaction $^{24}\text{Mg}(n, p)^{24}\text{Na}$. Magnesium carbonate is used, for example, as the target; the ^{24}Na is separated from the target by leaching out with water. This way of extracting radioactive isotopes has a restricted use, but owing to its simplicity often gives good results.

Equipment and Reagents

Equipment and Utensils. A counter for registering β - or γ -radiation. A source of neutrons ($F_s \geq 10^7$ neutron/s). A centrifuge. A lamp for evaporation. A flask with a long neck. A cupped planchet (flask) for irradiation. A porcelain bowl for 100 ml. Bowls for measuring the activity. A pipette with a syringe for 1-2 ml.

Reagents. MgO or $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3$. Ethanol (95 %). Solutions: 2 *N* HCl ; concentrated NH_4OH .

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons.

Irradiate 20-50 g of MgO (or MgCO_3) with neutrons in the planchet at an integral flux of at least 10^{12} . Pour the irradiated target into the long-neck flask in a glove box for working with dry radioactive substances. Extract the flask from the box and put it into the planchet under a hood. Leach out the ^{24}Na with water. To do this, incline the flask and, seeing that its contents are not splashed out, heat it 30 min with 100-150 ml of water. After cooling the liquid, pour it into the centrifuge tubes and centrifuge the solution, freeing it from solid particles. (If a floating film of precipitate remains, do not fear that the solution will become contaminated because the short-lived radioactive isotopes of magnesium will decay before you begin to measure the activity of the ^{24}Na .) Carefully evaporate the solution under a hood in the porcelain bowl, and then evaporate it until dry in a bowl for measuring the activity, and measure the activity of the ^{24}Na .

Dissolve the solid precipitate after leaching out in 2 *N* hydrochloric acid, avoiding a surplus of it, and precipitate $\text{Mg}(\text{NH}_4)_2(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$ from a definite portion of the solution. For this purpose, to a neutral solution containing 0.2 g of MgO per 50 ml of water, add an equal volume of 95% ethanol and 50 ml of a precipitating reagent [prepare the latter by saturating a mixture consisting of 18 ml of am-

monia, 75 ml of water, and 95 ml of 95% ethanol with solid $(\text{NH}_4)_2\text{CO}_3$]. Stir for 5 min, let the precipitate settle for 20 min, and separate the solution from it by centrifuging.

Evaporate the solution obtained in the porcelain bowl, and then evaporate it until dry in a bowl for measuring activity. Wet the dry residue in the bowl for measuring activity with concentrated nitric acid and dry it. Repeat this operation several times. (When heating the precipitate with nitric acid, avoid overheating.)

Measure the activity of the residue (a very small amount!) in a bowl. Reduce the results of measurement to the entire volume of the solution and to the time of measuring the activity of the preparation obtained as a result of leaching out. Calculate the fraction of the radioactive isotope of sodium extracted by simple boiling (leaching out). Determine the half-life of ^{24}Na and compare it with published data.

B. PREPARATION OF ^{32}P

Radioactive phosphorus can be prepared by the following reactions: $^{31}\text{P}(n, \gamma)^{32}\text{P}$; $^{32}\text{S}(n, p)^{32}\text{P}$, and $^{35}\text{Cl}(n, \alpha)^{32}\text{P}$. The last two reactions yield carrier-free ^{32}P , and they proceed only upon irradiation with fast neutrons.

Equipment and Reagents

Equipment and Utensils. A counter for registering β -particles. A source of neutrons ($F_s = 10^6$ - 10^7 neutron/s). A lamp for evaporation. An arrangement for distilling off carbon tetrachloride. A flask for irradiation (see Fig. 8.4). Beakers for 500, 200, and 100 ml. A sectional funnel for preparing precipitates for measuring activity.

Reagents. CCl_4 . Bromine water. Solutions: ammonium molybdate*; magnesia mixture**; Na_3PO_4 —5 and 40 mg/ml; concentrated of HNO_3 and H_2SO_4 .

-
- * This solution is intended for the precipitation of phosphate ion in the form of a salt of the heteropolyacid. To prepare it, dissolve 135 g of ammonium molybdate in 400 ml of water. Slowly pour the obtained solution while stirring into one litre of nitric acid (2 : 3). Let the solution stand, and then decant it.
- ** Magnesia mixture is intended for the precipitation of phosphate ion in the form of NH_4MgPO_4 . To prepare it, dissolve 50 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 100 g of NH_4Cl in 500 ml of water, acidify it with 1 ml of concentrated HCl , and add water to bring the volume of the solution up to one litre.

Performance of Work

(a) General Procedure

The flux of neutrons from the source must be known exactly. Take the cross section of the reactions $^{35}\text{Cl}(n, \alpha)^{32}\text{P}$ and $^{32}\text{S}(n, p)^{32}\text{P}$ from Appendix 9.

Use formula (8.2) to calculate the required amount of substance containing sulphur or chlorine and the duration of irradiation proceeding from the desired activity of the ^{32}P being obtained (take into account the geometric coefficient of the counter). It is expedient to obtain a preparation with an activity of 300-1000 cpm.

Put a substance containing sulphur or chlorine [H_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, CCl_4 , NaCl , etc.] into the flask for irradiation, introduce the neutron source into the centre of the flask, and keep it there during the calculated time. Register the time of the beginning and end of irradiation. Separate the ^{32}P from the irradiated target.

(b) Separation of ^{32}P from Irradiated H_2SO_4 (with an Isotope Carrier)

Dilute the irradiated concentrated sulphuric acid with water 10 times (pour the acid into the water!). Add 40 mg of sodium (or ammonium) phosphate to each 500 ml of the solution obtained as a carrier of the ^{32}P and precipitate the ammonium phosphomolybdate with heating up to 60°C using a considerable surplus of the ammonium molybdate solution (100 ml).

(c) Separation of ^{32}P from Irradiated CCl_4 (with an Isotope Carrier)

Transfer the irradiated carbon tetrachloride into the flask for distillation, add to it 10 ml of concentrated nitric acid, 5 mg of sodium phosphate, and an amount of water needed for the formation over the organic phase of a layer of water from 1 to 1.5 cm thick.

When carbon tetrachloride is irradiated, ^{32}P forms in the elementary state and in the form of tri- and pentavalent phosphorus. The elementary phosphorus is oxidized by the

nitric acid to phosphoric acid, while phosphorus chlorides are hydrolyzed by the water and are also oxidized to phosphoric acid.

Completely distil off the carbon tetrachloride. Pour the water layer into a beaker. A considerable part of the ^{32}P is on the walls of the flask used for irradiation. Therefore thoroughly wash the flask with hot concentrated nitric acid containing 2 mg of sodium phosphate. Add this solution to the main one. Next add 5 mg of sodium phosphate and precipitate the phosphate ion with the ammonium molybdate solution.

It is possible to precipitate ^{32}P in the form of MgNH_4PO_4 by adding the magnesia mixture to the solution obtained.

For this purpose, neutralize a nitric acid solution with ammonia (1:1) using a methyl red indicator. Add one or two drops of concentrated hydrochloric or nitric acid and 15-20 ml of a solution of the magnesia mixture (a 5-10-fold surplus) to the solution. Next, while continuously stirring with a glass rod, introduce a dilute (1:1) ammonia solution. When a white precipitate appears, stop adding the ammonia, but continue the stirring until the precipitate stops forming.

Now add a few more drops of ammonia, again stir the solution, and continue this procedure until the solution becomes alkaline. Add 15 ml more of ammonia (1:1), after which let the solution over the precipitate stand for 20-30 min, periodically stirring with the rod. It is desirable to cool the beaker containing the solution and precipitate with ice.

(d) Preparation of Sample for Measuring the Activity

Transfer the active precipitate prepared in one way or another quantitatively onto the paper filter of the sectional funnel for preparing the precipitates for activity measurement, dry the filter, and cover it with varnish.

Determine the half-life and the maximum energy of the β -particles. Compare the result obtained with published data.

C. PREPARATION OF ^{38}Cl

To prepare ^{38}Cl , one may use an (n, γ) reaction with sodium chlorate as the target (the solubility of sodium chlorate in water is ten times greater than that of potassium chlorate), as well as carbon tetrachloride or other organic chlorine-containing compounds.

At the expense of the recoil energy, part of the ^{38}Cl will appear in a chemical form other than that of the chlorine in the target. This makes it possible to separate a part of the ^{38}Cl from the target material. Isotope exchange between the separable form of the ^{38}Cl and the chlorine in the target material must be absent.

Equipment and Reagents

Equipment and Utensils. A counter for registering β -radiation. A source of neutrons ($F_s = 10^{7.5} \times 10^7$ neutron/s). A lamp for evaporation. A flask for irradiation (see Fig. 8.4). A beaker for 500 ml. Pipettes with syringes for 1 and 2 ml. A sectional funnel for preparing precipitates for activity measurement.

Reagents. Solutions: saturated NaClO_3 ; 0.01 M NaCl ; 0.05 M AgNO_3 ; 0.1 N and concentrated HNO_3 .

Performance of Work

Irradiate the saturated solution of sodium chlorate (for a group of students 1-1.5 litres may be irradiated) with neutrons in a laboratory source with an integral flux of the order of 2×10^{11} . Heat a definite part of the solution (100-200 ml) up to 70-90 $^{\circ}\text{C}$, add to the solution 9 ml of a 0.01 M solution of NaCl , 0.5 ml of concentrated nitric acid, and precipitate the chlorine in the form of AgCl , adding 2 ml of the 0.05 M solution of AgNO_3 .

Vigorously stir the precipitate to accelerate coagulation and filter it off in the sectional funnel for preparing precipitates for activity measurement. Wash the precipitate with a small amount of warm dilute (0.1 N) nitric acid, and then with water.

Determine the activity of the preparation during 40-80 min, performing measurements every 5-10 min. Use the results obtained to plot a graph in semilogarithmic coordinates and determine the half-life of the ^{38}Cl . Compare the result obtained with published data (see tables of isotopes).

Use isotope tables to determine what radioactive impurities the ^{38}Cl may contain and explain why they are present or absent.

D. PREPARATION OF ^{80}Br AND ^{82}Br

The radioactive bromine isotopes ^{80}Br (^{80m}Br) and ^{82}Br (^{82m}Br) are prepared by (n, γ) reactions from substances containing bromine. As a result of a nuclear reaction, nuclei of radioactive bromine receive recoil energy because of the emission of one or a series of γ -quanta. This energy is sufficient for breaking the chemical bond, as a result of which after irradiation the bromine may pass over into a chemical form other than that of the target, and owing to this can be separated from the entire mass of the target.

Equipment and Reagents

Equipment and Utensils. A counter for registering β - or γ -radiation. A source of neutrons. A lamp for evaporation. A paraffin block. A flask for irradiation. A separatory funnel for 1 litre. A sectional funnel for preparing precipitates for activity measurements. A measuring cylinder for 10 ml. A beaker for 100 ml.

Reagents. Ethyl bromide or bromobenzene. Solutions: 5% Na_2SO_3 ; 1% NaBr or KBr ; 0.05 M AgNO_3 ; 0.5 N HNO_3 .

Performance of Work

Pour about 0.5 litre of ethyl bromide (or bromobenzene) into the flask for irradiation. Place the flask in the paraffin block and irradiate it with an integral neutron flux of 10^{11} – 2×10^{11} . Pour the irradiated organic liquid into the separatory funnel and add to it 10 ml of a 5% solution of Na_2SO_3 and 1 ml of a 1% solution of NaBr . Shake the mixture during 0.5–1 min and separate the water fraction. Acidify the aqueous phase with 1 ml of 0.5 M HNO_3 . Precipitate the bromine in the form of AgBr with heating, adding 10 ml of a 0.05 M solution of AgNO_3 . Separate the precipitate on the paper filter of the sectional funnel for preparing precipitates for activity measurement. Wash the precipitate with 0.5 M HNO_3 . Dry the filter with the precipitate and cover it with varnish. All these manipulations must be performed in at most 30 min, therefore thoroughly prepare for this experiment.

Measure the activity of the preparation first every 5 min during 30-40 min, then every 30-60 min during six hours, and, finally, every 12-24 hours during 2-5 days.

Use the obtained data to plot the logarithm of the activity against the time. Find sections corresponding to ^{80m}Br , ^{80}Br , and ^{82}Br on the curve, determine the half-lives of each isotope and their activities at the instant of termination of the irradiation with neutrons. Find the relative yields of each isotope.

E. PREPARATION OF ^{128}I

The iodine isotope ^{128}I ($T_{1/2} = 24.99$ min) can be prepared by irradiating iodoorganic compounds with slow neutrons. At the expense of the recoil energy, part of the isotope ^{128}I is stabilized in a different chemical form in comparison with that of the target, which makes it possible to separate it from the mass of the target.

Equipment and Reagents

Equipment and Utensils. A counter for registering β -radiation. A source of neutrons ($F_s = 10^6$ neutron/s). A paraffin block. A lamp for evaporation. A flask for irradiation (see Fig. 8.4). A separatory funnel for 1 litre. A sectional funnel for preparing precipitates for activity measurement. A beaker for 500 ml.

Reagents. Iodine. Ethyl iodide. Solutions: 1% Na_2SO_3 ; 0.05 M AgNO_3 ; 2 N HNO_3 .

Performance of Work

Pour 0.5 litre of colourless ethyl iodide into the flask for irradiation. Insert the flask into the paraffin block. Irradiate the ethyl iodide during a time equal to 3-5 half-lives of ^{128}I .

After irradiation, add about 20 mg of elementary iodine to the ethyl iodide, and stir the contents of the flask well. Transfer the solution into the separatory funnel, and rinse the flask with 100 ml of water. Add the rinsing water to the solution in the separatory funnel. Add a freshly prepared solution of Na_2SO_3 to the mixture in an amount sufficient for decolourizing the iodine. Stir the mixture well and separate the water layer. Repeat the extraction with water twice. Combine the water extracts, acidify them with 10 ml

of a 2 *M* solution of HNO_3 , and heat the solution obtained. Precipitate the iodide ion with 10 ml of a 0.05 *M* solution of AgNO_3 . After coagulation, filter off the precipitate of AgI on the paper filter of the sectional funnel for preparing precipitates for activity measurement. Dry the filter (*be careful! the iodine may sublime*) and cover it with varnish. Perform all the operations as quickly as possible.

Measure the activity of the preparation every 5 min during one or two hours (the duration of measurement is 1 min). Determine the half-life of the ^{128}I and compare it with published data (see a table of isotopes).

F. PREPARATION OF ^{56}Mn

Radioactive Mn is prepared by the reaction $^{55}\text{Mn}(n, \gamma)^{56}\text{Mn}$. When an aqueous solution of potassium permanganate is irradiated with neutrons, ^{56}Mn is obtained mainly in the form of $^{56}\text{MnO}_2$ and $^{56}\text{Mn}^{2+}$. To separate the ^{56}Mn , inactive manganese(II) is usually added as a carrier. After acidification of the solution, manganese dioxide forms, which is easily separated from the entire mass of the target by simple filtration through a paper filter. Indeed, after the addition of Mn^{2+} , the manganese(II) in the acid medium reacts with the manganese(VII) to yield MnO_2 .

Equipment and Reagents

Equipment and Utensils. A counter for registering β - or γ -radiation. A source of neutrons ($F_s = 10^6$ neutron/s). A paraffin block. A flask for irradiation. A funnel for preparing precipitates for measuring activity. Beakers for 500 and 100 ml.

Reagents. Solutions: 5% KMnO_4 containing 20 ml of concentrated nitric acid per litre of solution; 0.5% MnSO_4 ; 12% NH_4OH ; 1% KCl .

Performance of Work

Irradiate 300 ml of a 5% solution of KMnO_4 containing HNO_3 with an integral flux of neutrons of 5×10^9 – 2×10^{10} . Pour the solution into a beaker and add 0.5 ml of a 0.5% solution of MnSO_4 to it. Neutralize the solution with 30 ml of a 12% solution of NH_4OH and vigorously stir it.

Filter off the formed manganese dioxide on the paper filter of the funnel for preparing precipitates for activity measurement. Wash the precipitate with small portions of a

1% solution of KCl (never use sodium or ammonium chloride).

Dry the filter with the precipitate, cover it with varnish, and place it into a tracing-paper envelope.

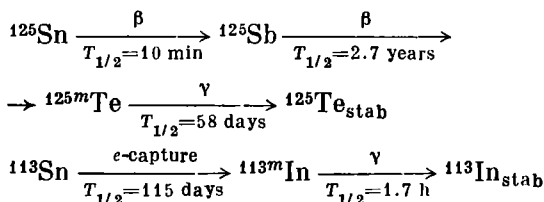
Identify the ^{56}Mn by determining its half-life. Calculate the possible activity of ^{40}K in the preparation.

Experiment 8.6. PREPARATION OF RADIOACTIVE ISOTOPES BY IRRADIATING TARGETS WITH NEUTRONS IN A NUCLEAR REACTOR [1, 6, 7]

The present experiment treats examples of separating radioactive isotopes from targets irradiated in a nuclear reactor, the radioactive isotopes being obtained by (n, γ) reactions with following β -decay.

A. SEPARATION OF ^{125}Sb BY INTERNAL ELECTROLYSIS FROM TIN IRRADIATED WITH NEUTRONS

The following radioactive isotopes of tin are obtained when metallic tin is irradiated with neutrons by (n, γ) reactions: ^{113}Sn , ^{117m}Sn , ^{119m}Sn , ^{121m}Sn , ^{123m}Sn , and ^{125}Sn . As a result of β -decay of ^{125}Sn and e -capture by ^{113}Sn , the isotopes ^{125}Sb , ^{125m}Te , and ^{113m}In accumulate in the target:



Consequently, the ^{125}Sb and ^{113m}In are in the target virtually without a carrier.

Equipment and Reagents

Equipment and Utensils. A counter for registering β - and γ -radiation. An arrangement for internal electrolysis (see Fig. 4.4). An analytical balance in a special glove box. A water bath. A soldering iron. A lamp for evaporation. Beakers for 50 ml (4). A porcelain bowl. Glass bowls for measuring activity. A glass plate 0.10×0.10 m in size. A crystallizer.

Radioactive Substances. Metallic tin in the form of a powder irradiated in a nuclear reactor at an integral neutron flux of the order of 10^{17} .

Reagents. Collodion. Solutions: transparent thermoplastic (Plexiglas) in dichloroethane; concentrated HNO_3 ; concentrated and 8 *M* HCl .

Performance of Work

Proceeding from the integral flux of neutrons, calculate what amount (in μCi) of ^{125}Sb is in 1 mg of the target (metallic tin) and what the total activity of the target is. Weigh an amount of the irradiated tin on the balance with an accuracy of within 0.001 g such that it contains 0.05-0.1 μCi of ^{125}Sb . Dissolve the weighed portion of the target in the cold in a minimum amount of aqua regia. Evaporate the solution on a water bath under a hood until it is almost dry. (*Caution! Antimony chlorides are volatile.*)

Dissolve the slightly moist residue in 3-5 ml of 8 *M* hydrochloric acid.

Bring the arrangement for internal electrolysis into its working state. For this purpose, first prepare the collodion membrane. Pour a portion of the collodion solution onto the glass plate and wait for 5-10 min. Next lower the glass together with the film into the crystallizer with water. The collodion film separates readily from the glass surface. The film prepared in this way can be stored several days in water.

Cut out a disk whose diameter corresponds to that of the Plexiglas tube from the film with scissors and glue it to the end of the tube with a solution of Plexiglas in dichloroethane. After a few minutes, fill the tube with water and check the tightness of the joint.

Use the soldering iron to solder the platinum wire with the plate of the electrolyzer to a metallic tin rod (the length of the rod is about 5 cm and its thickness is 0.3-0.5 cm). Insert the Plexiglas tube with the membrane and the tin rod into the rubber stopper. Insert the platinum cathode plate into the tube. Pour concentrated hydrochloric acid into a beaker and close it with the stopper in which the tube is fastened. Pour an 8 *M* solution of HCl containing ^{125}Sb into the tube (the cathode space) and note the time.

Perform internal electrolysis during 60 min. Extract the platinum plate and rapidly immerse it in distilled water.

Wash off the deposited antimony first with nitric, and then with hydrochloric acid. To do this, dip the plate in turn into a beaker with concentrated nitric acid, into one with water, and, finally, into a beaker with concentrated hydrochloric acid. Combine all three solutions and carefully evaporate them in a porcelain bowl on a water bath. When the volume of the solution becomes equal to 1 ml, transfer it into a glass bowl for activity measurement. Carefully evaporate the solution until dry under the lamp. Measure the activity of the obtained preparation in a counter with a known geometric coefficient. After introducing all the corrections, evaluate the yield of ^{125}Sb .

Identify the ^{125}Sb by determining the maximum energy of the β -particles or by measuring the γ -spectrum.

B. PREPARATION OF ^{131}I

Radioactive iodine (^{131}I) can be prepared by the following reaction: $^{130}\text{Te}(n, \gamma)^{131}\text{Te} \xrightarrow{\beta} ^{131}\text{I}$. The ^{131}I is easily separated from the target material by distillation.

Equipment and Reagents

Equipment and Utensils. A counter for registering the activity of a liquid with a scintillation detector of γ -radiation. An arrangement for distillation of ^{131}I (Fig. 8.6). An analytical balance in a special box. A water bath. A cylinder with nitrogen. Measuring cylinders for 5 ml (2). Glass test tubes for measuring the activity of a liquid in a scintillation counter.

Radioactive Substances. A Te or TeO_2 target irradiated in a nuclear reactor (the integral neutron flux must be known).

Reagents. Oxalic acid. Solutions: 9 M H_2SO_4 ; 50% chromic acid, 5% NaHCO_3 containing SO_2 .

Performance of Work

Use such an amount of Te or TeO_2 for the experiment that contains 37 MBq (1 μCi) of ^{131}I . Introduce the weighed sample into round-bottom flask 1 (Fig. 8.6) for distilling off the ^{131}I . Through separatory funnel 2 also pour into flask 1 a 9 M solution of H_2SO_4 and 50% chromic acid (at least 3 ml of sulphuric and 2 ml of chromic acid per every 0.5 g of tellurium). Heat the contents of the flask on the water bath up to complete dissolution of the target. The

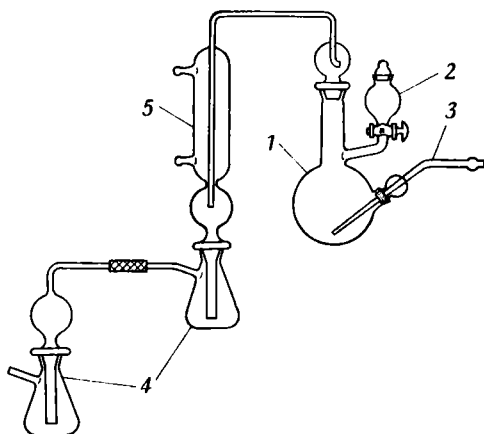


Fig. 8.6. Arrangement for distillation of ^{131}I :
 1—reaction flask; 2—funnel; 3—tube for passage of nitrogen;
 4—conical washing flask; 5—cooler

^{131}I passes over into iodate ion. Cool the solution and add a little more of the $9\text{ M H}_2\text{SO}_4$. Extract the separatory funnel and pour in about 2 mg of oxalic acid. The chromium(VI) is reduced to chromium(III), and elementary iodine forms. Pour 5-10 ml of the 5% solution of NaHCO_3 into each of the two conical flasks 4 and distil off all the ^{131}I with heating and with a small stream of nitrogen.

Measure the activity of a part of the solution in the γ -scintillation counter and evaluate the yield of ^{131}I . By measuring the half-life of the ^{131}I , verify its radiochemical purity.

Experiment 8.7. SEPARATION OF RADIOACTIVE ISOTOPES OBTAINED IN THE FISSION OF HEAVY NUCLEI [1, 8]

The experiment consists in separating and identifying the radioactive isotopes of iodine obtained in the irradiation of thorium or uranium with neutrons.

Equipment and Reagents

Equipment and Utensils. A counter for measuring β -particles. A source of neutrons ($F_s \geq 10^7$ neutron/s). A flask for irradiation with a capacity of 50 ml. A quartz device for distilling off iodine with water vapour with a capacity of 0.5 litre. A beaker for 200 ml. A sectional funnel for preparing precipitates for measuring the activity.

Radioactive Substance. $\text{Th}(\text{NO}_3)_4$ or $\text{UO}_2(\text{NO}_3)_2$ —150 g.

Reagents. NaNO_2 , NaNO_3 . Solutions: NaI (10 mg/ml); NaBr (10 mg/ml); 1 N H_2SO_4 ; 1 N NaOH ; 0.05 M AgNO_3 .

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons.

Using a table of the yield of fission products, determine the iodine isotopes that are obtained upon the fission of U (or Th) under the action of neutrons (see Fig. 8.1). Estimate which of these isotopes can be obtained in conditions of irradiation (with a given amount of natural thorium or uranium and a definite duration of irradiation from a laboratory source of neutrons).

Put 150 g of finely comminuted $\text{Th}(\text{NO}_3)_4$ [or $\text{UO}_2(\text{NO}_3)_2$] into the flask for irradiation and irradiate the substance with neutrons; the integral flux must be 5×10^{11} – 10^{12} . After this, transfer the salt into the flask of the device for distilling off iodine with water vapour and dissolve it in 150 ml of water. To the transparent solution add consecutively 1 ml of a solution of NaI (an iodine carrier), 1 ml of a solution of NaBr (a bromine carrier), 2.5 ml of 10% H_2SO_4 , and directly before closing the flask, 200 mg of NaNO_2 . Rapidly close the flask, immerse the end of the cooler into the receiver containing 100 ml of 1 N NaOH , a few minute crystals of Na_2SO_3 , and 1 ml of a solution of NaI . Cool the receiver with ice. Distil off the iodine oxidized to the elementary state with water vapour during half an hour after the solution begins to boil. Register the time of disappearance of the iodine vapour colour, assuming it to be the time of completion of the iodine distillation. Perform all the operations after distillation as fast as possible. After completing distillation, add 20 ml of 10% H_2SO_4 to the receiver for neutralizing the alkali and precipitate AgI by adding 2–3 ml of a 0.05 N solution of AgNO_3 .

Filter off the silver iodide and measure the activity of the dry preparation. Register the time of the first measure-

ment. Continue measuring the activity until its value becomes equal to that of the background. Plot in semilogarithmic coordinates a curve of the activity measurements against time and determine the half-lives of the separated iodine isotopes. For one of them, determine the value of the absolute activity at the instant of terminating irradiation. Calculate the amount of the found iodine isotope proceeding from the data on irradiation and the yield of the isotope in fission. By dividing this quantity by the one evaluated according to the data of irradiation, find the degree of separation of the given isotope.

Experiment 8.8. SEPARATION OF NUCLEAR ISOMERS OF ^{80}Br [1, 9]

When bromine is irradiated with neutrons, two nuclear isomers of ^{80}Br are obtained. The energy of the γ -quanta of an isomer transition is insufficient for a bromine recoil atom to break away from the parent molecule. But as a result of the emission of Auger electrons, the carbon-bromine bond is nevertheless broken. It therefore becomes possible to separate nuclear isomers.

Equipment and Reagents

Equipment and Utensils. A counter for the registration of β -particles. A source of neutrons ($F_s \geq 10^6$ neutron/s). A lamp for evaporation. A paraffin block with an opening for a flask. A Warren motor for 60 rpm. A high-voltage source with a kilovoltmeter. Two silver electrodes in the form of a disk and a platinum wire. Beakers for 1 litre and 200 ml. A flask for irradiation. A separatory funnel for 1 litre. A sectional funnel for preparing precipitates for activity measurement.

Reagents. Bromobenzene (or ethyl bromide). Solution: 1 % Na_2SO_3 ; NaBr (10 mg/ml); 0.5 N HNO_3 ; 0.05 M AgNO_3 .

Performance of Work

Before beginning the experiment, acquaint yourself without fail (!) with the rules for working with a source of neutrons (see Fig. 8.4).

Having placed the laboratory source of neutrons at the centre of the flask, irradiate 500 ml of ethyl bromide or bromobenzene during a time in which the integral flux will be 4×10^{10} ; the flask with the organic liquid must be in the

paraffin block (the flask may be surrounded with paraffin blocks).

Separate the entire radioactive bromine in the inorganic form, extracting it with 50 ml of a 1% solution of Na_2SO_3 containing 1 ml of NaBr (10 mg/ml). Separate the aqueous and organic fractions in the separatory funnel. Perform extraction three times, combining the water extracts (the first extract). Precipitate silver bromide by adding 3 ml of 0.5 N HNO_3 and 30 ml of a 0.05 M solution of AgNO_3 and filter the mixture on the sectional funnel for preparing precipitates for activity measurement. Perform all the operations as fast as possible.

Measure the activity first every two or three minutes during 40 min, and then every hour during 2-4 hours.

Divide the remaining organic fraction into two equal portions.

(a) Chemical Method of Separation

Keep the first part of the organic fraction for three hours and again extract the bromine with 150 ml of a 1% solution of NaNO_3 containing 1 ml of NaBr (10 mg/ml). Rapidly separate the aqueous phase (the second extract) and precipitate AgBr by adding 1 ml of 0.5 N HNO_3 and 10 ml of a 0.05 M solution of AgNO_3 . Filter off the precipitate on the sectional funnel. Measure the activity of the preparation every 3-5 min during 20-30 min (perform each measurement at most one minute). Determine the half-lives of the isotopes in the preparations obtained from the first and second extracts. Use the obtained half-lives to identify the isotopes in each preparation.

(b) Physical Method of Separation

Put the second part of the organic fraction into a beaker and hold it for two hours. Put the electrodes into the solution: a rotating silver disk coated on one side with varnish as the anode, and a platinum wire as the cathode. Perform electrolysis at a strength of the electric field equal to 10^4 V/m during 30 min. Extract the silver electrode and measure the change in its activity with time. Perform the measurement during four to eight hours.

Determine the half-life of the separated bromine and compare it with tabulated data.

Explain why the isomers separate.

Experiment 8.9. SEPARATION OF AN ISOTOPE FROM A TARGET IN A RADIOCHEMICALLY PURE STATE [1, 7]

The experiments are given below without a description of the procedure for separating an isotope from a target irradiated with nuclear particles.

In performing an experiment, follow a general rule. First draw up a scheme of separating or purifying the isotope. In establishing the procedure for running an experiment, it is good to use the most up-to-date ways of separating isotopes (chromatography, extraction, etc.). Check the radiochemical purity of an isotope using chemical (the method of carriers) and physical methods. In drawing up the plan for performing the experiment, calculate the protection from γ - and β -radiations of the isotopes and equip the workplace in accordance with the safety requirements.

Begin the practical running of an experiment only (!) after your instructor has approved the selected procedure for separation of the isotope from the target.

First separate or purify the isotope, and then prove its radiochemical purity and assay the yield of the separated isotope. Enter the results of the experiment in detail in your working record.

Example of Running an Experiment

It is required to obtain radioactive iron ^{59}Fe without an isotope carrier.

Radioactive iron can be obtained by irradiating metallic cobalt with fast neutrons in a nuclear reactor or a cyclotron. But metallic cobalt always contains a noticeable amount of iron, and therefore this way cannot be used to obtain ^{59}Fe without an isotope carrier. Cobalt salts, on the other hand, contain a small (0.0005%) amount of iron and, in addition, can be purified of it. At the same time, the irradiated target must not decompose when heated and intensively irradiated with neutrons, γ -quanta, and β -particles. The conclusion can be made from what has been said above that CoCl_2 is the best target.

Let us consider the scheme of separating $^{59}\text{Fe}^{\text{III}}$ without an isotope carrier from CoCl_2 (0.5 g) of a high purity irradiated during one day in a nuclear reactor.

First of all, we find in a table of isotopes the nuclear reaction used to obtain ^{59}Fe and by what secondary nuclear reactions other radioactive isotopes form from which the ^{59}Fe will have to be purified. Since cobalt chloride of a high purity is used as the target, we may take no account of the radioactive isotopes formed from the impurities present in the target material. Below are listed the nuclear reactions by which radioactive isotopes are obtained in the irradiated target:

$^{59}\text{Co} (n, \gamma) ^{60}\text{Co}$	$T_{1/2} = 5 \text{ years}$
$^{59}\text{Co} (n, p) ^{59}\text{Fe}$	$T_{1/2} = 45.1 \text{ days}$
$^{59}\text{Co} (n, \alpha) ^{56}\text{Mn}$	$T_{1/2} = 2.56 \text{ h}$
$^{59}\text{Co} (n, 2n) ^{58}\text{Co}$	$T_{1/2} = 72 \text{ days}$
$^{35}\text{Cl} (n, \gamma) ^{36}\text{Cl}$	$T_{1/2} = 3.1 \times 10^5 \text{ years}$
$^{37}\text{Cl} (n, \gamma) ^{38}\text{Cl}$	$T_{1/2} = 37.3 \text{ min}$
$^{35}\text{Cl} (n, p) ^{35}\text{S}$	$T_{1/2} = 87.1 \text{ days}$
$^{35}\text{Cl} (n, \alpha) ^{32}\text{P}$	$T_{1/2} = 14.3 \text{ days}$
$^{37}\text{Cl} (n, p) ^{37}\text{S}$	$T_{1/2} = 5 \text{ s}$
$^{37}\text{Cl} (n, \alpha) ^{34}\text{P}$	$T_{1/2} = 12 \text{ s}$

When the target is irradiated in a nuclear reactor, the ratio of the activity of the radioactive iron ^{59}Fe to that of cobalt ^{60}Co is 10^{-4} .

To diminish the activity of the ^{60}Co and of the isotopes produced by (n, γ) reactions, the target during the period of irradiation is wrapped in sheet cadmium 1 mm thick.

In these conditions, the ratio of the activity of the ^{59}Fe to that of the ^{60}Co diminishes somewhat. During the period of irradiation (24 h), about $10^{-5}\%$ of ^{36}Cl , 0.03% of ^{60}Co , 1% of ^{35}S , 2% of ^{59}Fe , and 5% of ^{32}P of the equilibrium amounts are obtained; the ^{56}Mn , ^{34}P , ^{37}S , and ^{38}Cl form in equilibrium amounts.

During the time of separation of the $^{59}\text{FeIII}$ from the target (about 3 h), the isotopes ^{34}P , ^{37}S , and ^{38}Cl will decay virtually completely, therefore their presence may be left out of consideration. Upon irradiation of the target with neutrons with a flux density of 10^{16} neutron/($\text{m}^2 \cdot \text{s}$) during a day, the isotope ^{36}Cl forms in such small amounts (~ 400 dps) that its presence can also be disregarded.

Consequently, when choosing the procedure for separating $^{59}\text{Fe}^{\text{III}}$ from a target, one must take into account the presence of the following radioactive impurities: $^{60}\text{Co}^{\text{II}}$, $^{56}\text{Mn}^{\text{II}}$, $^{32}\text{P}^{\text{V}}$, and $^{35}\text{S}^{\text{VI}}$.

Let us calculate the absolute activity of the ^{59}Fe that is obtained upon the irradiation during a day of 0.5 g of cobalt chloride in a nuclear reactor with a density of the fission neutron flux of 10^{16} neutron/($\text{m}^2 \cdot \text{s}$). The activation cross section of the reaction $^{59}\text{Co}(n, p)^{59}\text{Fe}$ on fission neutrons is 2×10^{-31} m^2/atom (2×10^{-3} barn). The build-up factor in the given case is $(1 - e^{-\lambda t}) = 0.02$. Hence, the absolute activity of the ^{59}Fe is 5×10^4 dps.

In a similar way, we can assay the activities of all the impurities.

The total activity of the target is 37-55 MBq (1.0-1.5 mCi); it is mainly due to the activity of the ^{60}Co . Assuming that the experiment will be run during three hours at a distance of 10 cm from the target, we can appraise the thickness of the required lead shielding. The thickness of the lead screen must be of the order of 3.5 cm.

To separate $^{59}\text{Fe}^{\text{III}}$ without a carrier from the radioactive impurities, it is good to use the extraction of iron with diisopropyl ether from an 8 *M* solution of HCl.

Let us track the entire process of separation and proof of the radiochemical purity.

The target is dissolved in water, carriers are added for the $^{32}\text{P}^{\text{V}}$, $^{35}\text{S}^{\text{VI}}$, and $^{56}\text{Mn}^{\text{II}}$ (Na_2HPO_4 , Na_2SO_4 , and MnSO_4) in amounts of 10-20 mg each; the ^{32}P and ^{35}P are oxidized with an alkaline solution of bromine or some other suitable oxidizing agent up to the formation of $^{32}\text{PO}_4^{3-}$ and $^{35}\text{SO}_4^{2-}$ ions, and next the manganese is reduced with oxalic acid in an acid medium to Mn^{2+} . The solution obtained is carefully evaporated until dry, the dry residue is dissolved in 8 *M* hydrochloric acid, and the $^{59}\text{Fe}^{\text{III}}$ is extracted with diisopropyl ether. The ether layer is separated and washed several times with an equal volume of 8 *M* hydrochloric acid, each volume containing 10-20 mg of inactive CoCl_2 , MnSO_4 , and Na_2HPO_4 . These salts are carriers of the radioactive ^{60}Co , ^{32}P , and ^{35}S , which could pass over into the organic phase, and anticarriers for ^{59}Fe . One thus succeeds in completely purifying the $^{59}\text{Fe}^{\text{III}}$ from radioactive impurities. The aqueous washing solutions must be retained. Next the $^{59}\text{Fe}^{\text{III}}$ purified from the radioactive impurities is

reextracted with 1 *N* hydrochloric acid, and a preparation is produced for performing the physical identification of the radioactive isotope.

A few milligrams of inactive iron(III) chloride are added to all the remaining aqueous washing solutions, and it is extracted several times with diisopropyl ether. This results in complete removal of the radioactive iron from the washing solutions. Cobalt and manganese are separated from these solutions by adsorption on a cation exchanger, and then phosphorus is precipitated in the form of MgNH_4PO_4 and sulphur in the form of BaSO_4 . After the cobalt and manganese ions are washed out with hydrochloric acid from the cation exchanger, the sulphides of these metals are precipitated. Preparations for activity measurement are obtained from the precipitates. The absence of radioactivity in the preparations obtained from the last washing solution indicates that the preparation of radioactive iron ^{59}Fe contains no impurities of ^{60}Co , ^{56}Mn , ^{32}P , and ^{35}S , and, consequently, is radiochemically pure.

Next physical methods are used to identify $^{59}\text{Fe}^{\text{III}}$. In the given case, it is difficult to measure the half-life during a short period of time. It is good practice to do this, however, if time allows.

A scintillation γ -spectrometer is used to measure the γ -spectrum of ^{59}Fe . It is difficult to determine the maximum energies of three series of β -particles for ^{59}Fe by the method of absorption of radiation in aluminium. If there is a β -spectrometer in the laboratory, one can determine the maximum energies of these three series of β -particles with sufficient accuracy.

The above example will help finding a correct approach to solving one of the problems given below.

A. NUCLEAR REACTIONS UNDER THE ACTION OF NEUTRONS

Nuclear reactors with a neutron (fast and slow) flux density of 10^{15} - 10^{17} neutron/($\text{m}^2 \cdot \text{s}$), cyclotrons with a neutron flux density of 10^{11} - 10^{13} neutron/($\text{m}^2 \cdot \text{s}$), and a laboratory source of neutrons with a flux of 5×10^6 - 5×10^7 neutron/s can be used as neutron sources.

Possible Variants of Experiments

(a) Separate carrier-free ^{32}P from irradiated solid NaCl and prove its purity.

(b) Separate carrier-free ^{35}S from irradiated solid NaCl and prove its purity.

(c) Separate carrier-free ^{45}Ca from irradiated solid ScCl_3 and prove its purity.

(d) Separate and identify carrier-free ^{56}Mn from irradiated FeSO_4 .

(e) Separate carrier-free ^{64}Cu from irradiated solid ZnCl_2 and prove its purity.

(f) Separate carrier-free ^{131}I from irradiated Na_2TeO_4 .

(g) Separate carrier-free ^{125}Sb from irradiated metallic Sn (not by internal electrolysis).

(h) Separate ^{24}Na from irradiated NaCl .

(i) Separate ^{42}K from an irradiated mixture of NaCl and KCl .

(j) Separate ^{64}Cu from irradiated solid CuSO_4 .

(k) Separate $^{76}\text{As}^{\text{V}}$ from an irradiated mixture of Na_3AsO_3 and Na_3SbO_3 .

(l) Separate ^{198}Au from an irradiated alloy of gold with copper and silver.

(m) Separate carrier-free $^{82,83}\text{Br}$ from irradiated solid $\text{UO}_2(\text{NO}_3)_2$.

(n) Separate carrier-free ^{95}Nb from irradiated solid $\text{UO}_2(\text{NO}_3)_2$.

(o) Separate carrier-free $^{127,129}\text{Te}$ from irradiated solid $\text{UO}_2(\text{NO}_3)_2$.

The neutron source for obtaining the required isotope is selected with a view to the effective cross section of the nuclear reaction. For running experiments (a), (b), (k), (l), and (m), the targets may be irradiated in a nuclear reactor, a cyclotron, or with the aid of a laboratory source; for running experiments (c), (f), (g), (h), (i), and (j), the targets should be irradiated in a cyclotron or a nuclear reactor; for running experiments (d) and (e), the targets must be irradiated in a nuclear reactor.

B. NUCLEAR REACTIONS UNDER THE ACTION OF DEUTERONS

The targets must be irradiated in a cyclotron with an ion current of the order of 10-100 μA at a deuteron energy of 10-20 MeV.

Possible Variants of Experiments

- (a) Separate ^{22}Na without a carrier from irradiated metallic Mg.
- (b) Separate carrier-free ^{48}V from irradiated TiO_2 .
- (c) Separate carrier-free ^{51}Cr from irradiated V_2O_5 or metallic V.
- (d) Separate carrier-free ^{52}Mn from irradiated CrO_3 or metallic chromium.
- (e) Separate carrier-free ^{56}Co from irradiated metallic Fe.
- (f) Separate carrier-free ^{65}Zn from irradiated metallic Cu.
- (g) Separate carrier-free ^{67}Ga from irradiated metallic zinc or ZnO .
- (h) Separate carrier-free ^{74}As from irradiated metallic germanium.
- (i) Separate carrier-free ^{181}W from irradiated metallic tantalum.
- (j) Separate ^{31}Si from irradiated SiO_2 .

C. NUCLEAR REACTIONS UNDER THE ACTION OF PHOTONS

The targets are irradiated in a betatron with a flux of photons having an energy of the order of 25 MeV.

Possible Variants of Experiments

- (a) Separate carrier-free ^{24}Na from irradiated magnesium chloride.
- (b) Separate carrier-free ^{56}Mn from irradiated iron vitriol.
- (c) Separate carrier-free ^{51}Co from irradiated nickel chloride.
- (d) Separate ^{76}As from irradiated elementary selenium.

Experiment 8.10. SEPARATION OF RADIOACTIVE ISOTOPES [1, 7]

The procedure of the experiment is worked out by the student independently according to published data.

Example of Performing an Experiment

Assume that it is necessary to separate radioactive silver from a nitric acid solution containing 37 kBq (1 μ Ci) each of ^{109}Cd and ^{110}Ag (both isotopes are with isotope carriers). When working with these amounts of isotopes during a working day (six hours), it is sufficient to use a lead glass screen 2 cm thick for shielding.

To separate the ^{110}Ag from the ^{109}Cd , it is necessary to precipitate the AgCl and separate the precipitate by centrifuging; the precipitate is first washed with a solution of inactive $\text{Cd}(\text{NO}_3)_2$, and then with water and is dissolved in ammonia. 10-20 mg of inactive $\text{Cd}(\text{NO}_3)_2$ are added to the solution and AgCl is again precipitated by heating the solution or neutralizing the ammonia. The precipitate is separated by centrifuging, and is washed first with an acid solution of inactive $\text{Cd}(\text{NO}_3)_2$, and then with water. The washing water is discarded. This process of reprecipitation is repeated several times, the obtained solutions being retained. AgCl is precipitated from the centrifugates by adding 10-20 ml of a solution of inactive AgNO_3 , and then hydrochloric acid. The precipitates are filtered off, and the filtrates are collected (separately). CdS is precipitated from these filtrates, and preparations are produced for measuring the activity. The absence of activity in these preparations (or in part of them) indicates that radioactive silver ^{110}Ag has been obtained in the radiochemically pure state.

It is difficult to measure the half-life of ^{110}Ag . It is simpler to measure the maximum energy of the β -particles and the spectrum of the γ -rays. It is also necessary to assay the yield of ^{110}Ag . [Mixtures of isotopes should contain activities of the order of 3.7-37 kBq (0.1-1 μ Ci) of each isotope.]

Possible Variants of Experiments

- (a) Separate radioactive ^{42}K from a mixture of ^{42}K and ^{24}Na (isotopes with carriers) and prove its purity.
- (b) Separate ^{32}P and ^{35}S (isotopes with carriers in the form of PO_4^{3-} and SO_4^{2-}) and prove their purity.
- (c) Separate ^{56}Mn from a mixture of ^{56}Mn and ^{59}Fe (isotopes with carriers) and prove its purity.
- (d) Separate ^{64}Cu from a mixture of ^{64}Cu and ^{65}Zn (isotopes with carriers) and prove its purity.
- (e) Separate ^{76}As from a mixture of ^{76}As and ^{124}Sb (isotopes with carriers in the solution in the form of AsCl_3 and HSbCl_6) and prove its purity.
- (f) Separate ^{82}Br and ^{131}I (carrier-free ^{131}I) and prove their purity.
- (g) Separate ^{89}Sr and ^{140}Ba (isotopes without or with a carrier) and prove their purity.
- (h) Separate ^{115}Cd and ^{111}In (isotopes with carriers) and prove their purity.
- (i) Separate ^{51}Cr and ^{59}Fe (isotopes with carriers) and prove their purity.
- (j) Separate $^{113,123}\text{Sn}$ and ^{124}Sb (isotopes with carriers) and prove their purity.
- (k) Separate ^{127}Te and ^{75}Se (isotopes with carriers) and prove their purity.
- (l) Separate ^{140}La and ^{141}Ce (isotopes with carriers) and prove their purity.
- (m) Separate ^{204}Tl and ^{110}Ag (isotopes with carriers) and prove their purity.
- (n) Separate ^{45}Ca and ^{89}Sr (isotopes with carriers) and prove their purity.
- (o) Separate ^{95}Zr and ^{95}Nb (isotopes without a carrier) and prove their purity.

Experiment 8.11. PURIFICATION

OF RADIOACTIVE ISOTOPES FROM RADIOACTIVE CONTAMINANTS [1, 7]

The procedure is worked out by the students independently according to published data.

Example of Performing an Experiment

A preparation of KCl contains 37 kBq (1 μ Ci) of ^{42}K and an admixture of ^{24}Na (the latter is about 1% with respect to activity). The ^{42}K is to be purified from the admixture of ^{24}Na .

Such an amount of the admixture ^{24}Na cannot be detected by measuring the activity of the ^{42}K because both isotopes have close half-lives; determination of the maximum energy of the β -particles or the spectrum of the γ -rays also does not make it possible to detect such an amount of the admixture.

To purify the ^{42}K , it is necessary to dissolve the preparation of KCl in water, add 50 mg of inactive NaCl, and treat the mixture with a solution of $[\text{Mg}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_8]$ (the magnesium-uranyl acetate must be thoroughly purified of UX_1 and UX_2). The precipitate of sodium-magnesium-uranyl acetate $[\text{NaMg}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}]$ is separated by centrifuging and is washed with a dilute solution of inactive KCl. The washing water is discarded.

50 mg of inactive NaCl are again added to the centrifugate containing a major part of the radioactive potassium and the precipitation of $[\text{NaMg}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}]$ is repeated. Both precipitates of the triple acetate are dissolved separately in a mineral acid and after the addition of 20 mg of inactive KCl to each solution (the activity of the ^{40}K may be disregarded), the sodium is again precipitated by neutralization with a solution of KOH. The precipitates are again reprecipitated in the presence of KCl.

Preparations for activity measurement are taken from both precipitates. The first precipitate will have an activity of the order of 0.37 kBq (0.01 μ Ci) associated with ^{24}Na ; the second precipitate should contain no activity. If activity is detected in the second precipitate, it is necessary to precipitate the sodium-magnesium-uranyl acetate from the initial solution containing ^{42}K a third time.

After the absence of activity in the second (or third) preparation of sodium-magnesium-uranyl acetate is proved (which indicates the radiochemical purity of the ^{42}K), a preparation of the ^{42}K is produced for measuring the half-life and for measuring the spectrum of the γ -rays and the maximum energy of the β -particles of the radioactive potassium.

All the work must be performed behind a screen made from lead glass.

Possible Variants of Experiments

In compiling assignments for purifying isotopes from radioactive contaminants, one must vary the activity of the contaminants within the range from 0.1 to 10% of the activity of the main isotopes. The total activity of the purified radioactive isotope should be 3.7-37 kBq (0.1-1 μ Ci).

- (a) Purify ^{89}Sr from ^{140}Ba and prove its purity.
- (b) Purify ^{65}Zn from ^{115}Cd and prove its purity.
- (c) Purify ^{115}Cd from ^{110}Ag and ^{114}In and prove its purity.
- (d) Purify ^{60}Co from ^{59}Fe and prove its purity.
- (e) Purify ^{59}Fe from ^{60}Co and ^{51}Cr and prove its purity.
- (f) Purify ^{124}Sb from ^{113}Sn and ^{127}Te and prove its purity.
- (g) Purify ^{141}Ce from ^{140}La , ^{143}Pr , and ^{147}Nd and prove its purity.
- (h) Purify ^{182}Ta from ^{185}W and prove its purity.
- (i) Purify ^{192}Ir from ^{197}Pt and prove its purity.
- (j) Purify ^{82}Br from ^{131}I and prove its purity.
- (k) Purify ^{32}P from ^{35}S and prove its purity.
- (l) Purify ^{35}S from ^{32}P and prove its purity.
- (m) Purify ^{24}Na from ^{35}S and ^{32}P and prove its purity.
- (n) Purify ^{42}K from ^{35}S and prove its purity.

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Chapter 9 Autoradiolysis of Radioactive Substances

THEORETICAL INTRODUCTION [1]

The **autoradiolysis** of radioactive substances is the proceeding of a number of chemical processes in them in storage as a result of the action of the corpuscular and electromagnetic radiation and of the recoil atoms formed in radioactive decay.

The studying of the chemical action of ionizing radiation on various substances is the subject of **radiation chemistry**. The autoradiolysis of radioactive substances is a border region between radiation chemistry and radiochemistry.

The basic quantitative characteristic of reactions proceeding under the action of ionizing radiation is their **radiation chemical yield** G . *It equals the number of molecules, ions, etc. formed (used up) when the system absorbs 100 eV of the energy of ionizing radiation.*

A knowledge of the radiation chemical yield of decomposition $G(-M)$ is of great significance because it characterizes the radiation stability of the molecules of a given substance. The degree of decomposition of a substance (the number of decomposed molecules) M with the molecular mass M at an absorbed dose D (in V/g), however, is determined not by the single quantity $G(-M)$, but by the product $G(-M)MD$.

This is why it is expedient to compare the radiation stability of substances not simply according to the values of $G(-M)$ found for identical values of D , but according to the products $G(-M)M$. For example, $G(-M)$ substantially decreases in ketones with an increase in their molecular mass, but the quantity $G(-M)M$ remains virtually the same for all studied ketones with a molecular mass from 72 to 142. Consequently, their radiation stability is also the same.

The values of $G(-M)$ are usually determined at low degrees of conversion of the substance being radiolyzed, i.e. at low absorbed doses. This is explained by the fact that at large doses the accumulation of the radiolysis products

stops being linear with respect to the dose owing to the proceeding of reactions with the primary radiolysis products of the initial substance. As a result, the quantity G ($-M$) stops being independent of the dose.

In the general case, the quantity G is evaluated by the equation

$$G = \frac{\Delta c N_A}{10D} \quad (9.1)$$

where Δc is the change in the concentration of the product (in mol/litre) when the substance absorbs a dose of D , eV/ml, and N_A is the Avogadro constant.

The absorbed dose (or dose rate) is calculated in various ways for autoradiolysis because the self-absorption of radiation by a substance depends on a number of factors: the type of radioactive decay, the configuration and size of the specimen, its state of aggregation, the characteristics of the medium, etc. Since the paths of β - and α -particles are usually much smaller than the dimensions of the vessel containing a preparation, the entire energy of these particles is absorbed by the preparation itself. At a small size of the preparation, the contribution of the energy of the γ -rays and antineutrinos attending decay is small and it may be ignored.

The dose rate of a β - or α -emitter with a specific activity of S (in Bq/g) and a mean particle energy of E (in MeV) is

$$P = 10^6 SE \text{ [eV/(g}\cdot\text{s)]} = 1.602 \times 10^{-10} SE \text{ [Gy/s]} \quad (9.2)$$

In the course of storage of a preparation, its activity S diminishes, therefore when calculating the dose rate one must take into account the change in the value of P_t in time. Since

$$S = S_0 e^{-\lambda t} \quad (9.3)$$

the expression for P_t becomes

$$P_t = 1.602 \times 10^{-10} S_0 E e^{-\lambda t} \quad (9.4)$$

Hence, the dose D (in Gy) absorbed by the preparation during the storage time t (in s) is

$$D = \frac{1.602 \times 10^{-10} S_0 E}{\lambda} (1 - e^{-\lambda t}) \quad (9.5)$$

where S_0 is the specific activity of the preparation at the beginning of storage, Bq/g, and λ is the decay constant, s^{-1} .

The maximum dose D_{∞} (in Gy) can be obtained upon the complete decay of a radioactive isotope, i.e. at $t \rightarrow \infty$. In this case,

$$D_{\infty} = \frac{1.602 \times 10^{-10} S_0 E}{\lambda} \quad (9.6)$$

The mechanism of autoradiolysis includes processes of intersection of radiation with a substance with the formation of unstable products of radiolysis (positive and negative ions, radicals, excited molecules) and the reactions of these primary products with one another and with the molecules of the medium leading to the formation of the radiolysis products.

If a radioactive preparation is an individual organic compound, its transformation as a result of autoradiolysis will be due to what is called the "direct" action of the radiation because the latter is absorbed directly by the given compound. On the other hand, the chemical transformations of a dilute solution of a radioactive substance are due to the "indirect" action of the radiation, i.e. to the reactions of this substance with the primary (and sometimes with the final) products of radiolysis of the solvent.

Finally, for concentrated solutions of a radioactive preparation, i.e. in binary and more complicated systems, autoradiolysis proceeds as a result of both direct and indirect action of the radiation.

The rate of radiation chemical processes (and, consequently, of autoradiolysis) depends on a number of parameters: the kind of ionizing radiation, the temperature, and the chemical composition of the system. The latter circumstance is of special significance because the introduction of additions of certain substances into a radioactive preparation makes it possible in a number of cases to appreciably diminish the depth of autoradiolysis or suppress the formation of undesirable products. The mechanism of the "protective" action of these additions consists in that they react with the primary products of radiolysis, suppressing the reactions of the latter with the radioactive substance or the reactions of formation of undesirable impurities.

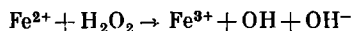
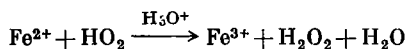
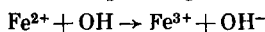
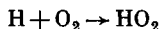
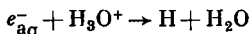
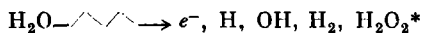
The possibility of radiolytic transformations must be taken into account not only when choosing the conditions of storing preparations with a considerable specific activity, but also when performing various chemical and biological

investigations with their use. The proceeding of radiation chemical reactions before the beginning and in the course of an investigation may lead to incorrect conclusions on the behaviour of a compound in the conditions of an experiment.

It must be noted that reactions under the action of radiation can also be used for the synthesis of radioactive substances.

Experiment 9.1. DETERMINING THE DOSE RATE OF RADIATION WITH A FERROUS SULPHATE DOSIMETER [1]

The greatest favour among the chemical methods of determining the dose rate of external sources of radiation has been given to the ferrous-sulphate dosimeter, often referred to as the Fricke dosimeter. It is a $(1-5) \times 10^{-3} M$ aqueous solution of Fe^{2+} in $0.4 M \text{H}_2\text{SO}_4$ containing $10^{-3} M \text{NaCl}$ and saturated with air. When radiation acts on this solution, the Fe^{2+} ions are oxidized to Fe^{3+} . The mechanism of this process consists in the following reactions:



The set of these reactions easily yields the following:

$$G(\text{Fe}^{3+}) = 3G(e_{\text{aq}}^-) + 3G(\text{H}) + G(\text{OH}) + 2G(\text{H}_2\text{O}_2) \quad (9.7)$$

The experimental value of $G(\text{Fe}^{3+}) = 15.6$ obtained for "hard" radiation coincides quite well with the values of the yields of the primary products of water radiolysis (at a pH from 0 to 2) found in various ways: $G(e_{\text{aq}}^-) = 3.05$, $G(\text{H}) = 0.6$, $G(\text{OH}) = 2.95$, $G(\text{H}_2\text{O}_2) = 0.8$.

At low energies of radiation, $G(\text{Fe}^{3+})$ diminishes, which is a result of the decrease in the quantities $G(e_{\text{aq}}^-)$, $G(\text{H})$, and $G(\text{OH})$. The matter is that when an ionizing particle passes through a medium, a multitude of events of ionization and

* The symbol $\text{---}/\text{---}/\text{---} \rightarrow$ signifies the action of radiation.

excitation of the medium's molecules occurs, most of these events occurring in local microregions (spurs) at a certain distance from one another. The distance diminishes with an increasing charge of an ionizing particle and (or) a decrease in its energy. When the spurs approach one another or overlap, the fraction of the primary products of radiolysis that have recombined into "molecular" products of radiolysis (in water— H_2 , H_2O_2 , H_2O) grows.

The value of $G(\text{Fe}^{3+}) = 15.6 \text{ mol}/100 \text{ eV}$ remains valid up to doses of $5 \times 10^3 \text{ Gy}^*$, does not virtually depend on the initial concentration of the Fe^{2+} in the solution in the range of 10^{-4} – 10^{-2} M , does not depend on the dose rate up to 10^6 Gy/s , and is virtually independent of the sulphuric acid concentration within the interval from 0.05 to 2.5 M . A change in the temperature from 0 to 70 °C also has no appreciable influence on $G(\text{Fe}^{3+})$.

The presence in a ferrous sulphate dosimetric solution of certain impurities (for example, ions of Br^- , alcohols) appreciably affects $G(\text{Fe}^{3+})$. To prevent this effect, it is recommended to prepare a dosimetric solution with the use of distilled water and reagents of analytically pure or chemically pure grades. In addition, NaCl is added to the solution because the Cl^- ions inhibit the action of organic impurities.

When performing dosimetry, the ferrous sulphate solution is poured into a vessel that is placed in a strictly definite position relative to the source of ionizing radiation. The dimensions and shapes of the vessels have virtually no influence on the process of oxidation of the Fe^{2+} ions if their internal diameter is larger than 8 mm. In the general case, the volume and configuration of the vessels for irradiation of the dosimetric solution are determined by the dimensions of the vessel for irradiation of the systems being studied.

There are different ways of determining the concentration of the Fe^{3+} ions in an irradiated dosimetric solution. The spectrophotometric method is in the greatest favour at present. According to this method, the differences between the optical densities ($\Delta\text{O.D.}$) of the irradiated and unirradiated solutions are determined at a wavelength of $\lambda = 304 \text{ nm}$ for various irradiation times t , and then $\Delta\text{O.D.}$ is plotted

* At large doses, $G(\text{Fe}^{3+})$ diminishes owing to the using up of the dissolved oxygen of the air.

versus t . This relation is linear up to doses at which the constancy of $G(\text{Fe}^{3+})$ still remains in force.

When determining the dose rate, it is good practice not to calculate the concentration of the Fe^{3+} ions, but to calculate directly the dose rate according to the following expression containing the concentration in the implicit form:

$$P = \frac{N_A (\Delta\text{O.D.}_{t_2} + \Delta\text{O.D.}_{t_1}) \times 100}{(\varepsilon_{\text{Fe}^{3+}} - \varepsilon_{\text{Fe}^{2+}}) G(\text{Fe}^{3+}) f \rho l (t_2 - t_1)} \quad (9.8)$$

where ε is the molar absorption or extinction coefficient; $\varepsilon_{\text{Fe}^{3+}} = 2197$ litre/(mol·cm), $\varepsilon_{\text{Fe}^{2+}} = 1$ litre/(mol·cm) at 25 °C and $\lambda = 304$ nm, f is a factor for converting electronvolts to grays ($f = 6.24 \times 10^{15}$ eV/Gy), ρ is the density of the dosimetric solution, $\rho = 1.024$ g/cm³, l is the length of the absorbing layer of the planchet, cm, and $t_2 - t_1$ is the time interval chosen on the linear section of the dependence of $\Delta\text{O.D.}$ on t , s.

For the kinds of radiation for which $G(\text{Fe}^{3+}) = 15.6$, at $l = 1$ cm formula (9.8) acquires the form

$$P = \frac{275 (\Delta\text{O.D.}_{t_2} - \Delta\text{O.D.}_{t_1})}{t_2 - t_1} \text{ Gy/s} \quad (9.9)$$

Very frequently a system being studied has characteristics of absorption differing from those for a ferrous sulphate system. In this case, the found value of P_f must be recalculated with regard to the given object. For systems consisting of atoms of light elements and for a photon energy of 0.1-3.0 MeV, recalculation is performed by the formula

$$P_s = \frac{F_s P_f}{F_f} \quad (9.10)$$

where F_s and F_f are the electron densities of the system being studied and the dosimetric system, respectively.

The values of F are calculated by the formula

$$F = N_A \left(p_1 \frac{Z_1}{A_1} + p_2 \frac{Z_2}{A_2} + \dots + p_n \frac{Z_n}{A_n} \right) \quad (9.11)$$

where p_i is the mass fraction in the system of the element with an atomic mass of A_i and an atomic number of Z_i .

273 Experiment 9.1

Equipment and Reagents

Equipment and Utensils. A spectrophotometer. A pipette for 1 ml. Glass ampoules with an internal diameter of 8 mm and a volume of 2 ml closed with a rubber tube having a glass stopper (15).

Source of Radiation. Isotope γ -installations or an electron accelerator can be used as the source of radiation.

Reagents. Distilled water. Chemically pure or analytically pure concentrated sulphuric acid with a density of 1.84 g/cm³. $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ of an analytically pure grade, recrystallized from a solution of purified sulphuric acid. Chemically pure or analytically pure NaCl.

Performance of Work

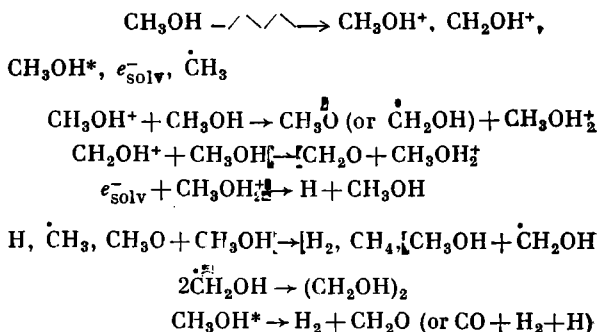
Preparation of a Dosimetric Solution and Filling of the Ampoules. Dissolve 0.4 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or 0.5-0.6 g of Mohr's salt, 50-60 mg of NaCl, and 22 ml of sulphuric acid in 1 litre of distilled water. Rinse the ampoules with the prepared solution, after which pour 1 ml of the solution into each ampoule and close it with a rubber tube provided with a stopper.

Irradiation and Analysis. Irradiate the specimens consecutively (three specimens at a time) with five different doses. Calculate the duration of the exposure proceeding from the fact that at the longest exposure the optical density of the irradiated solution will not exceed 1. After irradiation, determine the optical density at $\lambda = 304 \text{ nm}$ of the irradiated solutions with respect to the unirradiated one ($\Delta\text{O.D.}$) and plot $\Delta\text{O.D.}$ against the irradiation time t . Choose two values of O.D. corresponding to two different irradiation times t on the linear section of this relation, and then calculate P_t and P_s by formulas (9.9)-(9.11).

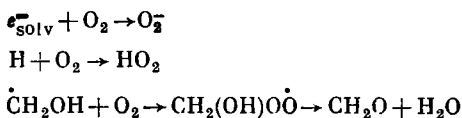
Experiment 9.2. AUTORADIOLYSIS OF LABELLED METHANOL [2, 3]

The given experiment shows the mechanism of autoradiolytic processes occurring during the storage of labelled compounds taking a very simple organic compound as an example. The simplified mechanism of methanol radiolysis in-

cludes the following set of reactions:



The addition to methanol of substances that are highly reactive with respect to certain primary products of radiolysis appreciably affects the yields of the final products. For example, if methanol contains O_2 , ethylene glycol does not form, $G(\text{H}_2)$ sharply drops, while $G(\text{H}_2\text{O})$ increases. The explanation is that O_2 is an acceptor of radicals, solvated electrons, and excited molecules:



Hence, a preparation of methanol, depending on the specific activity, time and conditions of storage, the nature and position of the tracer atom ($^{14}\text{CH}_3\text{OH}$, CT_3OT , CT_3OH , CH_3OT), will contain a certain amount of impurities consisting of the autoradiolysis products.

Equipment and Reagents

Equipment and Utensils. A radiochromatograph with a detector according to the heat of combustion or the thermal conductivity provided with a device for breaking open ampoules. A vacuum installation. Glass ampoules with a diameter of 8 mm and a volume of 2 ml with a constriction for sealing off (20). A pipette for 1 ml. A syringe for 1 ml with a needle. A Dewar flask for 1 litre.

Source of Radiation. The same as in Experiment 9.1.

Radioactive Substances. Methanol $^{14}\text{CH}_3\text{OH}$ with a specific activity about 4 MBq/g (10 mCi/g).

Reagents. Methanol, hydrogen, methane, liquid nitrogen.

Performance of Work

The experiment is performed in two stages. The first stage includes preparation of the specimens and irradiation, the second—analysis of the specimens and processing of the results.

Preparation of Specimens. Use the pipette to pour 1 ml of unlabelled methanol into each of 10 ampoules, and of labelled methanol into each of the other 10 ampoules. Evacuate in turn 7 specimens each of the labelled and unlabelled methanol by repeating three or four cycles of freezing-pumping off-unfreezing. Upon the completion of evacuation (when the vacuum reaches an order of 0.132 Pa), seal off the frozen specimens at the places of the constrictions. Seal off the remaining six specimens also in the frozen state, but without evacuation. See that the constrictions at the instant of sealing are clean (without traces of frozen methanol).

Irradiation. Irradiate four evacuated specimens of each kind of alcohol within the interval up to 10^{18} – 10^{19} eV/g. Hold the remaining specimens without irradiation during a month at room temperature.

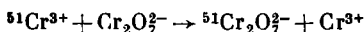
Analysis. Use radiochromatography to analyse all the specimens in turn for their content of hydrogen and methane. With the aid of a model gas mixture containing hydrogen, methane, and air in the proportion of 10:1:89, plot a calibrating graph of the dependence of the area of the chromatogram peaks on the corresponding volumes of methane and hydrogen. Find the volume of the radiolytic gases according to this graph.

Perform analysis and calibration in the following conditions: a column 4 m long and 6 mm in diameter with Grade ASM silica gel and at room temperature; the rate of flow of the carrier gas is 20 ml/min.

Use the data obtained to plot product accumulation curves, i.e. the dependences of the volumes of the gases on the absorbed dose. Calculate the values of $G(\text{H}_2)$ and $G(\text{CH}_4)$ in the irradiated specimens by formula (9.1) using the accumulation curves. Compare the results with one another.

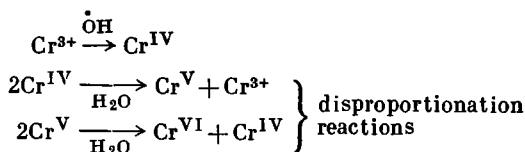
Experiment 9.3. RADIOLYTIC TRANSFORMATIONS OF ^{51}Cr IN AN AQUEOUS SOLUTION

The object of the present experiment is to show the possibility of erroneous conclusions on the physicochemical properties of the system being studied if the own radiation of the labelled atoms is not taken into account. Assume that we want to see if the exchange of chromium atoms between $\text{Cr}_2(\text{SO}_4)_3$ and $\text{K}_2\text{Cr}_2\text{O}_7$ is possible in an acid solution. This problem can be solved by studying the distribution of ^{51}Cr in the system $^{51}\text{Cr}_2(\text{SO}_4)_3\text{-K}_2\text{Cr}_2\text{O}_7$. To establish the presence of isotope exchange in this system, it is evidently necessary to measure the activity in Cr^{III} and Cr^{VI} immediately after mixing the salts, one of which contained ^{51}Cr , and then repeat the measurement in a sufficiently long time. If the specific activity and the time of holding the mixture are great, atoms of ^{51}Cr will be found to appear in the $\text{K}_2\text{Cr}_2\text{O}_7$. Hence the conclusion can be drawn that the slow spontaneous exchange of chromium atoms is possible between $\text{Cr}_2(\text{SO}_4)_3$ and $\text{K}_2\text{Cr}_2\text{O}_7$:

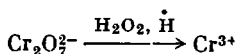


This is not correct, however. The fact that part of the activity passed over from the $^{51}\text{Cr}^{3+}$ to the $\text{Cr}_2\text{O}_7^{2-}$ is explained by the appearance of hydrated electrons e_{aq}^- , radicals $\cdot\text{OH}$, $\cdot\text{H}$, and hydrogen peroxide in the aqueous solution under the action of the radiation of the ^{51}Cr .

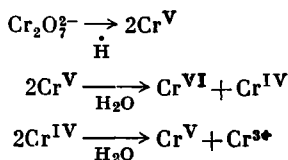
The $\cdot\text{OH}$ radicals oxidize the $^{51}\text{Cr}^{3+}$:



The $\text{Cr}_2\text{O}_7^{2-}$ ions can be reduced by the atomic hydrogen and hydrogen peroxide:



or by stages:



It is easy to see that the effect of the transfer of the activity from one oxidation state to the other is due to radiation, and not to isotope exchange by subjecting a specimen to the action of radiation from an external source.

Equipment and Reagents

Equipment and Utensils. A counter with a detector of γ -radiation. A chromatographic column filled with the cation exchanger SDV-3. Conical flasks for 10 ml (10). A pipette for 5 ml with a syringe.

Source of Radiation. The same as in Experiment 9.1.

Radioactive Substances. Cr_2O_3 containing ^{51}Cr with a specific activity of 1×10^3 MBq/g (300 mCi/g).

Reagents. A 0.01 M solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.5 M H_2SO_4 .

Performance of Work

Add 10 mg of $^{51}\text{Cr}_2\text{O}_3$ to 5 ml of a 0.01 M solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.5 M H_2SO_4 . Use the chromatographic column with the ion-exchange resin to separate $\text{K}_2\text{Cr}_2\text{O}_7$ from the mixture of salts of Cr^{III} and Cr^{VI} . Determine the specific activity of the bichromate. Analyse another specimen prepared in a similar way after several (5-8) weeks of storage. Irradiate a third specimen immediately after preparing it up to a dose of 10^{19} eV/ml, after which separate the $\text{K}_2\text{Cr}_2\text{O}_7$ and determine its specific activity. Compare the results of all three measurements.

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1. Pikaev, A. K. *Dosimetriya v radiatsionnoi khimii* (Dosimetry in Radiation Chemistry). Moscow, Atomizdat (1975).
2. Baxendale, I. H. and Wardman, P. *The Radiolysis of Methanol: Product Yields, Rate Constants, and Spectroscopic Parameters of Intermediates*. NSRDS, National Bureau of Standards (1975).
3. Skraba, W. I., Burr, J. G., and Hess, D. N., *J. Phys. Chem.* **21**: 1296 (1953).

Appendices

1. SELECTED IMPORTANT CONSTANTS

Charge of electron . . .	$e = 4.80_3 \times 10^{-10} \text{ cgse}_q = 1.60_2 \times 10^{-19} \text{ C}$
Rest mass of electron	$m_e = 9.10_9 \times 10^{-31} \text{ kg}$
Rest mass of proton . .	$m_p = 1.672_6 \times 10^{-27} \text{ kg}$
Mass of hydrogen atom	$m_H = 1.673_9 \times 10^{-27} \text{ kg} = 1.0081_9 \text{ amu}$
Ratio of proton mass to electron mass	$m_p/m_e = 183_6$
Rest mass of neutron . .	$m_n = 1.674_9 \times 10^{-27} \text{ kg} = 1.0088_8 \text{ amu}$
Atomic mass unit . . .	$\text{amu} = 1.660_5 \times 10^{-27} \text{ kg}$
Ratio of physical atomic mass to chemical atomic mass	$k_A = 1.000 \text{ } 27_2$
Avogadro constant . . .	$N_A = 6.022_1 \times 10^{26} \text{ kmol}^{-1}$
Loschmidt number (number of molecules per cubic centimetre at STP)	$N_L = N_A/V_{\text{mol}} = 2.687 \times 10^{19} \text{ cm}^{-3}$
Volume of mole of a gas at STP	$V_{\text{mol}} = 22.41_4 \times 10^3 \text{ cm}^3$
Planck constant	$h = 6.62_6 \times 10^{-34} \text{ J}\cdot\text{s}$
Boltzmann constant . .	$k = R/N_A = 1.380_6 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$
Molar gas constant . .	$R = 8.314_4 \times 10^3 \text{ J}\cdot\text{K}^{-1} \text{ kmol}^{-1} = 1.986_5 \text{ cal}\cdot\text{K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9648_4 \text{ C}\cdot\text{equiv}^{-1}$
Speed of light	$c = 2.9979_2 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
Density of air (at STP)	$\rho = 1.29_3 \text{ kg}\cdot\text{m}^{-3}$
Absolute zero of temperature	$0 \text{ K} = -273.15 \text{ }^\circ\text{C}$
Curie	$1 \text{ curie} = 3.70 \times 10^{10} \text{ dps} = 2.222 \times 10^{12} \text{ dpm} = 3.7 \times 10^{10} \text{ Bq}$
1 year = 365.2422 days = 8765.8135 h = 5.2595 $\times 10^5$ min = 3.1557 $\times 10^7$ s	
1 day = 24 h = 1440 min = 0.864 $\times 10^5$ s	

2. INTERNATIONAL TABLE OF ATOMIC MASSES *

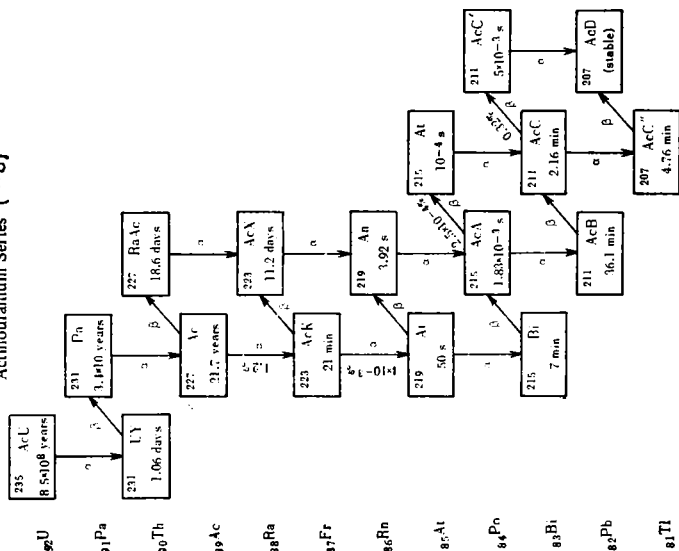
Element	Symbol	Atomic number	Atomic mass	Element	Symbol	Atomic number	Atomic mass
Actinium	Ac	89	(227)	Erbium	Er	68	167.2 ₆
Aluminium	Al	13	26.98154	Europium	Eu	63	151.96
Americium	Am	95	(243)	Fermium	Fm	100	(253)
Antimony	Sb	51	121.7 ₅	Fluorine	F	9	18.99840
Argon	Ar	18	39.94 ₈	Francium	Fr	87	(223)
Arsenic	As	33	74.9216	Gadolinium	Gd	64	157.25
Asatine	At	85	(210)	Gallium	Ga	31	69.72
Barium	Ba	56	137.34	Germanium	Ge	32	72.5 ₉
Berkelium	Bk	97	(247)	Gold	Au	79	196.9665
Beryllium	Be	4	9.01218	Hafnium	Hf	72	178.49
Bismuth	Bi	83	208.9804	Helium	He	2	4.00260
Boron	B	5	10.81	Holmium	Ho	67	164.9304
Bromine	Br	35	79.904	Hydrogen	H	1	1.0079
Cadmium	Cd	48	112.41	Indium	In	49	114.82
Calcium	Ca	20	40.08	Iodine	I	53	126.9045
Californium	Cf	98	(251) *	Iridium	Ir	77	192.2 ₂
Carbon	C	6	12.011	Iron	Fe	26	55.84 ₇
Cerium	Ce	58	140.12	Krypton	Kr	36	83.80
Cesium	Cs	55	132.9054	Lanthanum	La	57	138.905 ₅
Chlorine	Cl	17	35.453	(Lawrencium)	(Lr)	103	(257)
Chromium	Cr	24	51.996	Lead	Pb	82	207.2
Cobalt	Co	27	58.9332	Lithium	Li	3	6.94 ₁
Copper	Cu	29	63.54 ₆	Lutetium	Lu	71	174.96 ₇
Curium	Cm	96	(247)	Magnesium	Mg	12	24.305
Dysprosium	Dy	66	162.5 ₀	Manganese	Mn	25	54.9380
Einsteinium	Es	99	(254)	Mendelevium	Md	101	(258)

Element	Symbol	Atomic number	Atomic mass	Element	Symbol	Atomic number	Atomic mass
Mercury	Hg	80	200.5 _a	Samarium	Sm	62	150.4
Molybdenum	Mo	42	95.94	Scandium	Sc	21	44.9559
Neodymium	Nd	60	144.24	Selenium	Se	34	78.9 _a
Neon	Ne	10	20.17 _a	Silicon	Si	14	28.085 _s
Neptunium	Np	93	237.0482	Silver	Ag	47	107.868
Nickel	Ni	28	58.71	Sodium	Na	11	22.98977
Niobium	Nb	41	92.9064	Strontium	Sr	38	87.62
Nitrogen	N	7	14.0067	Sulphur	S	16	32.06
Nobelium	No	102	(254)	Tantalum	Ta	73	180.947 _a
Osmium	Os	76	190.2	Technetium	Tc	43	98.9062*
Oxygen	O	8	15.999 ₄	Tellurium	Te	52	127.6 _a
Palladium	Pd	46	106.4	Terbium	Tb	65	158.9254
Phosphorus	P	15	30.97376	Thallium	Tl	81	204.3 _a
Platinum	Pt	78	195.0 _a	Thorium	Th	90	232.0381
Plutonium	Pu	94	(242)	Thulium	Tm	69	168.9342
Polonium	Po	84	(209)*	Tin	Sn	50	118.6 _a
Potassium	K	19	39.098 _a	Titanium	Ti	22	47.90
Praseodymium	Pr	59	140.9077	Tungsten	W	74	183.85
Promethium	Pm	61	(145)*	Uranium	U	92	238.02 _a
Protactinium	Pa	91	231.0359	Vanadium	V	23	50.9415
Radium	Ra	88	226.0254	Xenon	Xe	54	131.30
Radon	Rn	86	(222)	Ytterbium	Yb	70	173.0 ₄
Rhenium	Re	75	186.207	Yttrium	Y	39	88.9059
Rhodium	Rh	45	102.9055	Zinc	Zn	30	65.38
Rubidium	Rb	37	85.467 _s	Zirconium	Zr	40	91.22
Ruthenium	Ru	44	101.0 ₇				

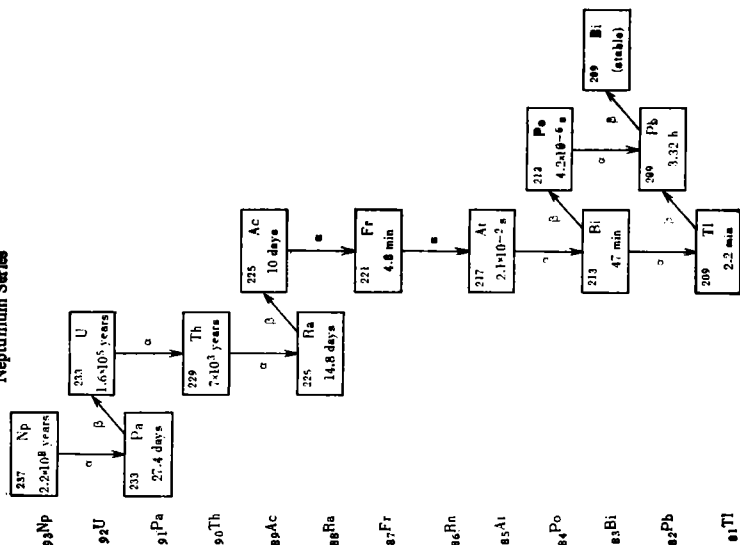
* The values of the atomic masses are given in the ¹²C scale according to official data (1977). The numbers in parentheses denote the atomic mass numbers of the most stable or best known (noted by an asterisk) isotopes.

3. Radioactive Series

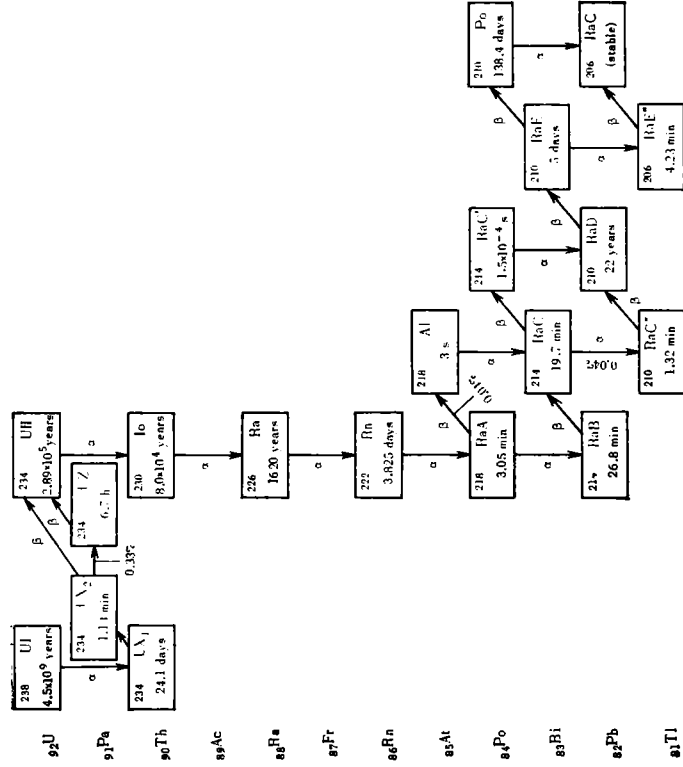
Actinouranium Series (^{235}U)



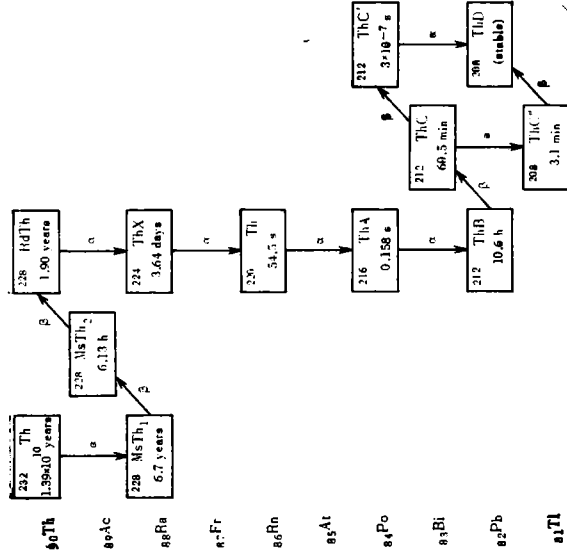
Neptunium Series



Uranium-Radium Series



Thorium Series



**4. VALUES OF t_{γ}
FOR DIFFERENT CONFIDENCE LEVELS γ**

Number of de- grees of freedom f	Confidence level γ				Number of de- grees of freedom f	Confidence level γ			
	0.90	0.95	0.99	0.999		0.90	0.95	0.99	0.999
1	6.314	12.706	63.657	636.619	18	1.734	2.101	2.878	3.922
2	2.920	4.303	9.925	31.598	19	1.729	2.093	2.861	3.883
3	2.353	3.182	5.841	12.941	20	1.725	2.086	2.845	3.850
4	2.132	2.776	4.604	8.610	21	1.721	2.080	2.831	3.819
5	2.015	2.571	4.032	6.859	22	1.717	2.074	2.819	3.792
6	1.943	2.447	3.707	5.959	23	1.714	2.069	2.807	3.767
7	1.895	2.365	3.499	5.405	24	1.711	2.064	2.797	3.745
8	1.860	2.306	3.355	5.041	25	1.708	2.060	2.787	3.725
9	1.833	2.262	3.250	4.781	26	1.706	2.056	2.779	3.707
10	1.812	2.228	3.169	4.587	27	1.703	2.052	2.771	3.690
11	1.796	2.201	3.106	4.437	28	1.701	2.048	2.763	3.674
12	1.782	2.179	3.055	4.318	29	1.699	2.045	2.756	3.659
13	1.771	2.160	3.012	4.221	30	1.697	2.042	2.750	3.646
14	1.761	2.145	2.977	4.140	40	1.684	2.021	2.704	3.551
15	1.753	2.131	2.947	4.073	60	1.671	2.000	2.660	3.460
16	1.746	2.120	2.921	4.015	120	1.658	1.980	2.617	3.373
17	1.740	2.110	2.898	3.965	∞	1.645	1.960	2.576	3.291

5. VALUES OF χ^2 FOR 5% SIGNIFICANCE LEVEL

Number of degrees of freedom f	$\chi^2_{0.05}$	Number of degrees of freedom f	$\chi^2_{0.05}$	Number of degrees of freedom f	$\chi^2_{0.05}$
1	3.841	13	22.362	25	37.652
2	5.991	14	23.685	26	38.885
3	7.815	15	24.996	27	40.113
4	9.488	16	26.296	28	41.337
5	11.070	17	27.587	29	42.557
6	12.592	18	28.869	30	43.773
7	14.067	19	30.144	32	46.194
8	15.507	20	31.410	34	48.602
9	16.919	21	32.671	36	50.998
10	18.307	22	33.924	38	53.384
11	19.675	23	35.172	40	55.758
12	21.026	24	36.415		

**6. DETERMINATION OF TOTAL NUMBER OF COUNTS ENSURING A GIVEN ACCURACY
OF REGISTERING RADIOACTIVITY AT A 95% CONFIDENCE LEVEL**

$\frac{I_{s+b}}{I_b}$	$\delta_{0.95}=1\%$		$\delta_{0.95}=2\%$		$\delta_{0.95}=3\%$		$\delta_{0.95}=5\%$		$\delta_{0.95}=10\%$	
	N_b	N_{s+b}	N_b	N_{s+b}	N_b	N_{s+b}	N_b	N_{s+b}	N_b	N_{s+b}
1.3	920 000	1 350 000	230 000	340 000	110 000	150 000	37 000	54 000	9 200	14 000
1.5	350 000	630 000	86 000	160 000	38 000	70 000	14 000	26 000	3 500	6 300
1.7	190 000	400 000	46 000	100 000	21 000	45 000	7 300	16 000	1 900	4 000
2.0	93 000	270 000	24 000	66 000	11 000	30 000	3 700	11 000	930	2 700
3.0	26 200	140 000	6 600	34 000	3 000	16 000	1 100	5 500	270	1 400
5.0	7 800	87 000	2 000	22 000	860	9 800	310	3 500	80	870
7.0	3 900	72 000	1 000	18 000	430	8 000	160	2 900	40	720
10.0	2 200	63 000	500	16 000	220	7 000	80	2 500	20	630
20.0	600	54 000	150	14 000	70	6 000	30	2 200	6	540
30.0	300	49 000	80	13 000	40	5 400	12	2 000	3	490
50.0	130	46 000	40	12 000	15	5 100	6	1 900	—	460
100.0	50	43 000	11	11 000	5	4 800	—	1 800	—	430
500.0	4	41 000	—	11 000	—	4 500	—	1 700	—	410

7. LABORATORY SOURCES OF NEUTRONS *

Radioactive isotope	Half-life	Nuclear reaction	Radiation obtained	Energy of neutrons, Mev	Flux of neutrons per curie of isotope, s ⁻¹
²²⁶ Ra	1590 years	² Be(α , n) ¹² C	n, γ	up to 13	1.7×10^7
²²⁶ Ra	1590 years	¹¹ B(α , n) ¹¹ N	n, γ	up to 6	6.7×10^6
²²² Rn	3.825 days	⁹ Be(α , n) ¹² C	n, γ	up to 11	
²¹⁰ Po	138.4 days	⁹ Be(α , n) ¹² C	n	up to 8	2.3×10^6
²³⁹ Pu	2.4×10^4 years	⁹ Be(α , n) ¹² C	n, γ	up to 11	2.2×10^6
²²⁶ Ra	1590 years	⁹ Be(γ , n) ⁸ Be	n, γ	0.12 and 0.51	3.3×10^4
¹²⁴ Sb	60 days	⁹ Be(γ , n) ⁸ Be	n, γ	0.02	1.9×10^5
²⁴ Na	14.8 h	⁹ Be(γ , n) ⁸ Be	n, γ	0.8	1.4×10^5
²⁴ Na	14.8 h	² H(γ , n) ¹ H	n, γ	0.220	2.9×10^5
¹⁴⁰ Ba— ¹⁴⁰ La	13.4 days; 40 h	⁹ Be(γ , n) ⁸ Be	n, γ	0.620	2.2×10^3
¹⁴⁰ Pa— ¹⁴⁰ La	13.4 days; 40 h	² H(γ , n) ¹ H	n, γ	0.140	7.4×10^4
²²⁷ Ac	21.7 years	⁹ Be(α , n) ¹² C	n, γ	—	2.1×10^7
²⁵² Cf	2.631 years	Fission	n, γ	—	1.3×10^{10}

* The neutron yield by the reaction n, γ is given for 1 g of the target substance (Be or D₂O) at a distance of 1 cm from the source.

8. CAPTURE CROSS SECTIONS OF THERMAL NEUTRONS

Isotope capturing neutrons				Capture cross section, barn	
Atomic number	Element	Mass number	Content in natural mixture of isotopes, %	For pure isotope	For natural mixture
8	O	18	0.204	0.0002	4×10^{-7}
9	F	19	100	0.0094	0.0094
11	Na	23	100	0.50	0.50
12	Mg	26	11.29	0.060	0.0054
13	Al	27	100	0.21	0.21
14	Si	30	3.13	0.155	0.00485
15	P	31	100	0.19	0.19
16	S	34	4.18	0.26	0.011
17	Cl	35	75.4	41	30
		37	24.6	0.56	0.137
19	K	41	6.729	1.0	0.067
20	Ca	44	2.13	0.61	0.013
		48	0.179	0.58 (*)	0.00105 (*)
		48	0.179	0.216	0.00039
21	Sc	45	100	22	22
22	Ti	50	5.34	0.141 (*)	0.0075 (*)
		50	5.34	0.039	0.0021
23	V	51	100	4.50	4.50
24	Cr	50	4.31	11.6	0.50
		54	2.38	0.059	0.00014
25	Mn	55	100	10.7	10.7
26	Fe	58	0.34	0.294	0.0010
27	Co	59	100	0.66 (*)	0.66 (*)
		59	100	21.7	21.7
28	Ni	64	1.16	1.49	0.0173
29	Cu	63	68.94	2.90	2.0
		65	31.06	1.80	0.26
30	Zn	64	48.89	0.53	0.26
		68	18.61	1.02	0.19
		68	18.61	0.29 (*)	0.054 (*)
31	Ga	69	60.16	1.40	0.855
		71	39.84	3.25	1.30
32	Ge	70	20.55	0.46	0.095
		74	36.74	0.39	0.14
		76	7.67	0.072	0.0055
33	As	75	100	4.2	4.2
34	Se	74	0.86	3.3	0.2
		80	49.62	20.46	0.23
		80	49.62	0.034 (*)	0.017 (*)
		82	9.39	0.060	0.0056
35	Br	79	50.61	8.1	4.1
		79	50.51	2.76 (*)	1.39 (*)
		81	49.49	2.25	1.11

Isotope capturing neutrons				Capture cross section, barn	
Atomic number	Element	Mass number	Content in natural mixture of isotopes, %	For pure isotope	For natural mixture
37	Rb	85	72.8	0.72	0.52
		87	27.2	0.122	0.033
38	Sr	86	9.75	1.29	0.128
		88	82.74	0.0050	0.00415
39	Y	89	100	1.24	1.24
40	Zr	94	17.5	0.42	0.073
		96	2.9	0.31	0.009
41	Nb	93	100	1.0	1.0
42	Mo	100	9.63	0.457	0.044
		98	23.78	0.42	0.10
		92	15.84	0.0063	0.001
44	Ru	104	18.27	0.668	0.122
		102	31.34	1.18	0.37
45	Rh	103	100	137	137
		103	100	11.6 (*)	11.6 (*)
46	Pd	108	26.8	11.2	3.0
		110	13.5	0.39	0.0525
47	Ag	107	51.35	44.8	23
		109	48.65	94 ⁽⁰⁾	45.6 ⁽⁰⁾
		109	48.65	2.3	1.1
48	Cd	114	28.75	1.1	0.30
		114	28.75	0.14 (*)	0.040 (*)
		116	7.63	1.4	0.10
		113	12.30	0.4	0.05
49	In	113	4.23	59.6 (*)	2.52
		115	95.77	50.6 (*)	49.5 (*)
		115	95.77	144.1	138
50	Sn	112	0.9	1.3	0.012
		112	0.9	1.58 (*)	0.0042 (*)
		120	33.03	0.22	0.072
		124	6.11	0.147	0.009
51	Sb	124	6.11	0.638 (*)	0.039 (*)
		121	57.25	6.6	3.8
		123	42.75	2.6	1.1
52	Te	126	18.83	0.81	0.15
		126	18.53	0.076 (*)	0.014 (*)
		128	32.57	0.134	0.0436
		128	32.57	0.0155 (*)	0.00504(*)
		130	34.11	0.216	0.0735
		130	34.11	0.009 (*)	0.003 (*)
53	I	127	100	6.25	6.25
55	Cs	133	100	0.016 (*)	0.016 (*)
		133	100	25.6	25.6
		138	71.66	0.511	0.367

Isotope capturing neutrons				Capture cross section, barn	
Atomic number	Element	Mass number	Content in natural mixture of isotopes, %	For pure isotope	For natural mixture
57	La	139	99.911	8.4	8.4
59	Pr	141	100	10.1	10.1
62	Sm	154	22.53	5.0	1.10
		152	26.63	135	35.8
		144	3.16	0.253	0.008
63	Eu	151	47.77	1450	681
		153	52.23	747	390
64	Gd	158	24.96	3.6	0.9
65	Tb	159	100	10.7	10.7
66	Dy	164	28.18	2590	725
		164	28.18	117 (*)	33 (*)
67	Ho	165	100	59.6	59.6
69	Tm	169	100	106	106
71	Lu	175	97.5	16.3	15.9
		176	2.5	3640	91.0
72	Hf	180	35.11	10.0	3.5
73	Ta	181	100	0.034 (*)	0.034 (*)
		181	100	20.6	20.6
74	W	184	30.68	2.09	0.64
		186	29.17	34.9	10.2
75	Re	185	37.7	103	38.5
		187	62.93	73.9	46.5
76	Os	192	40.97	1.61	0.66
		190	26.38	0.29	2.19
77	Ts	191	38.5	260 (*)	100 (*)
		191	38.5	1000	388
		193	61.5	128	79.0
78	Pt	196	26.6	1.1	0.30
		198	7.2	3.92	0.292
79	Au	197	100	96.4	96.4
80	Hg	204	6.7	0.34	0.0228
		202	29.6	2.45	0.725
81	Tl	203	29.46	0.268	0.079
		205	70.54	3.15	2.2
83	Bi	209	100	0.015	0.015

Note. * The capture cross sections of thermal neutrons were measured according to the artificial radioactivity of the products of a nuclear reaction.

The above data may have an error of $\pm 10-20\%$ and relate to neutrons having a speed of 2200 m/s.

An asterisk (*) indicates the cross section for a reaction in which a nuclear isomer is obtained at the highest energy level.

The symbol (°) indicates the cross section for a reaction producing a nuclear isomer with a shorter half-life.

**9. YIELD OF ISOTOPES FOR
MOST IMPORTANT NUCLEAR REACTIONS UNDER
THE ACTION OF PROTONS, DEUTERONS,
AND α -PARTICLES**

Isotope	Nuclear reaction	Energy of particles, MeV	Yield, $\mu\text{Ci}/(\mu\text{A} \cdot \text{h})$	Isotope	Nuclear reaction	Energy of particles, MeV	Yield, $\mu\text{Ci}/(\mu\text{A} \cdot \text{h})$
^7Be	$\text{Li} (n, p)$	22	170	^{62}Zn	$\text{Zn} (p, 2n)$	22	18 000
^7Be	$\text{Li} (d, 2n)$	15	48	^{65}Zn	$\text{Cu} (p, n)$	22	11
		30	150	^{66}Zn	$\text{Cu} (d, 2n)$	15	38
^{11}C	$\text{B} (d, n)$	8	500			30	20
^{18}F	$\text{F} (p, np)$	22	7 500	^{67}Ga	$\text{Zn} (p, 2n)$	22	590
^{18}F	$\text{O} (\alpha, pn)$	38	5 000	^{67}Ga	$\text{Zn} (d, n)$	15	58
^{22}Na	$\text{Na} (p, pn)$	22	3.1			30	700
^{22}Na	$\text{Mg} (d, \alpha)$	30	2.0	^{68}Ge	$\text{Ga} (p, 2n)$	30	3 600
^{24}Na	$\text{Al} (d, p\alpha)$	30	2 200			22	26
^{27}Mg	$\text{Al} (d, \alpha)$	30	48 000	^{71}Ge	$\text{Ga} (d, 2n)$	19	8
^{35}S	$\text{Cl} (d, \alpha)$	19	8.4	^{74}As	$\text{Ge} (p, n)$	22	170
^{42}K	$\text{Ca} (d, \alpha)$	19	3.3	^{74}As	$\text{Ge} (d, 2n)$	30	80
^{45}Ca	$\text{Ti} (d, \alpha)$	19	0.01	^{77}Br	$\text{Se} (p, 2n)$	22	1 100
^{45}Ti	$\text{Sc} (p, n)$	22	10^5	^{82}Br	$\text{Se} (d, 2n)$	19	500
^{48}V	$\text{Ti} (p, n)$	22	590	^{79}Kr	$\text{Br} (p, n)$	22	2 600
^{48}V	$\text{Ti} (d, 2n)$	15	75	^{86}Rb	$\text{Sr} (d, \alpha)$	14	1.0
		30	350			30	20
^{51}Cr	$\text{V} (d, 2n)$	19	0.2	^{85}Sr	$\text{Rb} (d, 2n)$	15	16
		30	280			19	0.60
	$\text{V} (p, n)$	22	450		$\text{Rb} (p, n)$	22	63.8
^{52}Mn	$\text{Cr} (p, n)$	22	80	^{88}Y	$\text{Sr} (p, n)$	22	52
^{52}Mn	$\text{Cr} (d, 2n)$	15	144		$\text{Sr} (d, 2n)$	15	38
		30	400	^{89}Zn	$\text{Y} (d, 2n)$	30	58
^{54}Mn	$\text{Cr} (p, n)$	22	0.5			14	7.0
^{54}Mn	$\text{Mn} (p, pn)$	22	20			19	75.0
^{54}Mn	$\text{Fe} (d, \alpha)$	15	14		$\text{Y} (p, n)$	22	1 900
		30	5	^{90}Nb	$\text{Mo} (d, \alpha)$	14	2.4
^{55}Fe	$\text{Mn} (p, n)$	22	10	^{92m}Nb	$\text{Zr} (p, n)$	22	100
^{55}Fe	$\text{Mn} (d, 2n)$	15	37	^{95}Nb	$\text{Mo} (d, \alpha)$	14	0.08
		30	10	^{99}Mo	$\text{Zr} (d, n)$	38	0.1
^{59}Fe	$\text{Co} (d, 2p)$	30	2	^{103}Pd	$\text{Rh} (p, n)$	22	520
^{58}Co	$\text{Fe} (p, n)$	20	70	^{105}Ag	$\text{Pb} (p, n)$	22	29
^{58}Co				^{109}Cd	$\text{Ag} (d, 2n)$	15	2.6
and						30	2.7
^{57}Co	$\text{Fe} (d, 2n)$	30	39		$\text{Ag} (p, n)$	22	5.3
^{57}Co	$\text{Fe} (d, n)$	15	9.5	^{111}In	$\text{Cd} (p, n)$	22	230
^{57}Co	$\text{Ni} (p, pn)$	22	50		$\text{Cd} (d, 2n)$	15	48
^{64}Cu	$\text{Zn} (d, 2p)$	19	300	$^{111-114}\text{In}$	$\text{Cd} (\alpha, pxn)$	19	0.1
	$\text{Zn} (d, \alpha)$	30	1 200	^{113}Sn	$\text{Cd} (\alpha, xn)$	38	0.5
^{67}Cu	$\text{Zn} (d, 2p)$	30	15	^{119}Sb	$\text{Sn} (p, 2n)$	22	2 600

Isotope	Nuclear reaction	Energy of particles, MeV	Yield, $\mu\text{Ci}/(\mu\text{A} \cdot \text{h})$	Isotope	Nuclear reaction	Energy of particles, MeV	Yield, $\mu\text{Ci}/(\mu\text{A} \cdot \text{h})$
^{125}I	$\text{Tl} (p, 2n)$	22	40	^{188}Ir	$\text{Os} (p, 2n)$	22	1 000
^{131}I	$\text{Tl} (d, n)$	8	2	$^{193\text{m}}\text{Pt}$	$\text{Ir} (p, n)$	22	270
^{133}Ba	$\text{Cs} (d, 2n)$	14	20	^{194}Au	$\text{Pt} (p, 2n)$	22	2 000
		14	100	^{195}Au	$\text{Pt} (p, 2n)$	22	12
^{139}Ce	$\text{La} (d, 2n)$	15	3.1	^{201}Tl	$\text{Hg} (p, 2n)$	22	820
^{139}Pr	$\text{Ce} (p, 2n)$	22	56 000	^{203}Pb	$\text{Tl} (p, n)$	22	220
^{140}Nd	$\text{Pr} (p, 2n)$	22	3 600	^{206}Bi	$\text{Pb} (p, n)$	22	320
^{181}W	$\text{Ta} (d, 2n)$	15	4.5		$\text{Pb} (d, 2n)$	30	850

**10. ACTIVATION CROSS SECTIONS OF (n, p)
AND (n, α) REACTIONS ON FISSION NEUTRONS**

Reaction	Cross section, mbarn	Reaction	Cross section, mbarn
$^{24}\text{gM}(n, p)^{24}\text{Na}$	1.3	$^{54}\text{Fe}(n, p)^{54}\text{Mn}$	66
$^{27}\text{Al}(n, p)^{27}\text{Mg}$	3.43	$^{56}\text{Fe}(n, p)^{56}\text{Mn}$	0.44
$^{27}\text{Al}(n, \alpha)^{24}\text{Na}$	0.6	$^{54}\text{Fe}(n, \alpha)^{51}\text{Cr}$	0.37
$^{31}\text{P}(n, p)^{31}\text{Si}$	31	$^{59}\text{Co}(n, p)^{59}\text{Fe}$	0.25
$^{32}\text{S}(n, p)^{32}\text{P}$	60	$^{59}\text{Co}(n, \alpha)^{56}\text{Mn}$	0.14
$^{33}\text{S}(n, \alpha)^{31}\text{Si}$	3	$^{58}\text{Ni}(n, p)^{58}\text{Co}$	105
$^{35}\text{Cl}(n, p)^{35}\text{S}$	16	$^{58}\text{Ni}(n, \alpha)^{55}\text{Fe}$	0.17
$^{35}\text{Cl}(n, \alpha)^{32}\text{P}$	3	$^{65}\text{Cu}(n, p)^{65}\text{Ni}$	0.64
$^{39}\text{K}(n, \alpha)^{36}\text{Cl}$	3	$^{64}\text{Zn}(n, p)^{64}\text{Cu}$	39
$^{42}\text{Ca}(n, p)^{42}\text{K}$	3.3	$^{67}\text{Zn}(n, p)^{67}\text{Cu}$	0.9
$^{45}\text{Sc}(n, p)^{45}\text{Ca}$	40	$^{68}\text{Zn}(n, \alpha)^{65}\text{Ni}$	0.02
$^{54}\text{Sc}(n, \alpha)^{42}\text{K}$	0.2	$^{74}\text{Se}(n, p)^{74}\text{As}$	5
$^{46}\text{Ti}(n, p)^{46}\text{Sc}$	13	$^{92}\text{Mo}(n, p)^{92}\text{Nb}$	6.2
$^{47}\text{Ti}(n, p)^{47}\text{Sc}$	22	$^{103}\text{Rh}(n, p)^{103}\text{Ru}$	0.093
$^{51}\text{V}(n, \alpha)^{48}\text{Sc}$	0.08	$^{110}\text{Cd}(n, p)^{110}\text{Ag}$	0.1
		$^{132}\text{Ba}(n, p)^{132}\text{Cs}$	5.3

11. ABSORPTION COEFFICIENTS OF β -RAYS IN ALUMINIUM

Atomic number of element Z	Element	Mass number of isotope	Half-life	Decay constant λ , s ⁻¹	Energy of electrons, MeV	Absorption coefficient in aluminium, cm ² /g
11	Na	24	14.94 h	0.128×10^{-4}	1.390, 4.17	8.1
15	P	32	14.295 days	0.561×10^{-6}	1.708	5.3
16	S	35	87.1 days	0.921×10^{-7}	0.169	290
17	Cl	38	37.29 min	0.310×10^{-3}	1.11, 2.77, 4.81	8.7, 3.2
19	K	42	12.44 h	0.155×10^{-4}	2.07; 3.58	2.56
20	Ca	45	163 days	0.492×10^{-7}	0.254	128
25	Mn	56	2.574 h	0.747×10^{-4}	0.75, 1.05, 2.86	4.85
26	Fe	59	47.1 days	0.170×10^{-6}	0.271, 0.462, 1.560	43
27	Co	60	4.95 years	0.444×10^{-8}	0.306	79
29	Cu	64	12.88 h	0.149×10^{-4}	0.571	33
		66	5.10 min	0.226×10^{-3}	1.59, 2.63	3.2
30	Zn	65	250 days	0.321×10^{-7}	0.325*	107
33	As	76	1.115 days	0.719×10^{-5}	0.48, 1.76, 2.413, 2.969	4.3
35	Br	80	18 min	0.642×10^{-3}	0.7, 1.1, 1.97	6.4
		82	1.495 days	0.537×10^{-5}	0.181, 0.323, 0.447	35
37	Rb	86	19.5 days	0.411×10^{-6}	0.716, 0.811	6.7
38	Sr	89	54.5 days	0.147×10^{-6}	1.463	8.8
39	Y	90	2.54 days	0.316×10^{-5}	2.270	4.7
40	Zr	95	65 days	0.123×10^{-6}	0.360, 0.405, 0.910	60
42	Mo	99	2.8 days	0.286×10^{-6}	0.445, 1.225	13.7

Atomic number of element Z	Element	Mass number of isotope	Half-life	Decay constant λ , s^{-1}	Energy of electrons, MeV	Absorption coefficient in aluminium, cm^2/g
45	Rh	104	41.8 s	0.166×10^{-1}	2, 2.6	3.9
47	Ag	108	2.44 min	0.473×10^{-2}	1.15, 1.77	6.7
		110	24.2 s	0.286×10^{-1}	2.24, 2.82	2.9
		110	270 days	0.297×10^{-7}	0.088, 0.520, 2.885	36.5
48	Cd	115	2.2 days	0.365×10^{-5}	0.600, 1.120	10.7
51	Sb	124	60 days	0.134×10^{-5}	0.48, 0.65, 1.0, 1.62, 2.37	14
53	I	128	24.99 min	0.462×10^{-3}	1.59, 2.02	5.33
55	Cs	134	2.3 years	0.955×10^{-8}	0.085, 0.280, 0.420, 0.650	23
57	La	140	1.65 days	0.486×10^{-5}	1.32, 1.67, 2.26	9.6
66	Dy	165	2.319 h	0.830×10^{-4}	0.3, 1.25	12.4
81	ThC'		3.1 min	0.373×10^{-3}	1.805	8
82	ThB		10.67 h	0.182×10^{-4}	0.365, 0.589	56.7
82	RaB		26.8 min	0.431×10^{-3}	0.350, 0.670, 0.726, 0.779	29
82	RaD		22 years	0.100×10^{-8}	0.0167, 0.0556	2034
82	AcB		36.1 min	0.320×10^{-3}	0.571, 1.40	341
83	RaE		4.989 days	0.161×10^{-5}	1.17	17
83	ThC		1.09 h	0.191×10^{-3}	0.45, 0.62, 2.20	5.3
90	UY		1.066 days	0.753×10^{-5}	0.093, 0.216, 0.302	111
90	UX ₁		24.101 days	0.333×10^{-6}	0.103, 0.193	170
91	UX ₂		1.175 min	0.098×10^{-2}	0.600, 1.500, 2.320	6.7
91	UZ		6.7 h	0.287×10^{-4}	0.45, 1.2	100

* Energy of positrons.

12. RELATIONS BETWEEN DIFFERENT UNITS OF ENERGY MEASUREMENT

	MeV	amu	erg	g	kW·h	cal	M.K.S.
1 MeV	1	1.074×10^{-3}	1.602×10^{-6}	1.782×10^{-27}	4.45×10^{-20}	3.827×10^{-14}	1.633×10^{-14}
1 amu	0.931×10^3	1	1.49×10^{-3}	1.66×10^{-24}	4.15×10^{-17}	3.565×10^{-11}	1.519×10^{-10}
1 erg	6.24×10^5	6.70×10^{-2}	1	1.113×10^{-21}	2.78×10^{-14}	2.389×10^{-8}	1.019×10^{-8}
1 g*	5.61×10^{26}	6.02×10^{23}	8.986×10^{20}	1	2.50×10^7	2.447×10^{13}	0.916×10^{13}
1 kW·h	5.75×10^7	6.17×10^4	3.60×10^{13}	4.01×10^{-8}	1	8.60×10^5	3.670×10^5
1 cal	2.612×10^{13}	2.804×10^{10}	4.1855×10^7	4.658×10^{-14}	1.16×10^{-6}	1	0.4267
1 M.K.S.	0.612×10^{14}	0.658×10^{19}	0.981×10^8	1.092×10^{-13}	2.725×10^{-6}	2.344	1

* The energy equivalent to a mass of 1.g ($E = mc^2$).

13. VALUES OF FUNCTIONS e^x AND e^{-x}

x	e^x	e^{-x}	x	e^x	e^{-x}	x	e^x	e^{-x}
0.00	1.0000	1.0000	0.45	1.5683	0.6376	0.90	2.4596	0.4066
0.01	1.0101	0.9900	46	1.5841	0.6313	91	2.4843	0.4025
02	1.0202	0.9802	47	1.6000	0.6250	92	2.5093	0.3985
03	1.0305	0.9704	48	1.6161	0.6188	93	2.5345	0.3946
04	1.0408	0.9608	49	1.6323	0.6126	94	2.5600	0.3906
0.05	1.0513	0.9512	0.50	1.6487	0.6065	0.95	2.5857	0.3867
06	1.0618	0.9418	51	1.6653	0.6005	96	2.6117	0.3829
07	1.0725	0.9324	52	1.6820	0.5945	97	2.6379	0.3791
08	1.0833	0.9231	53	1.6989	0.5886	98	2.6645	0.3753
09	1.0942	0.9139	54	1.7160	1.5827	99	2.6912	0.3716
0.10	1.1052	0.9048	0.55	1.7333	0.5769	1.00	2.7183	0.3679
11	1.1163	0.8958	56	1.7507	0.5712	01	2.7456	0.3642
12	1.1275	0.8869	57	1.7683	0.5655	02	2.7732	0.3606
13	1.1388	0.8781	58	1.7860	0.5599	03	2.8011	0.3570
14	1.1503	0.8694	59	1.8040	0.5543	04	2.8292	0.3535
0.15	1.1618	0.8607	0.60	1.8221	0.5488	1.05	2.8577	0.3499
16	1.1735	0.8521	61	1.8404	0.5434	06	2.8864	0.3465
17	1.1853	0.8437	62	1.8589	0.5379	07	2.9154	0.3430
18	1.1972	0.8353	63	1.8776	0.5326	08	2.9447	0.3396
19	1.2092	0.8270	64	1.8965	0.5273	09	2.9743	0.3362
0.20	1.2214	0.8187	0.65	1.9155	0.5220	1.10	3.0042	0.3329
21	1.2337	0.8106	66	1.9348	0.5169	11	3.0344	0.3296
22	1.2461	0.8025	67	1.9542	0.5117	12	3.0649	0.3263
23	1.2586	0.7945	68	1.9739	0.5066	13	3.0957	0.3230
24	1.2712	0.7866	69	1.9937	0.5016	14	3.1268	0.3198
0.25	1.2840	0.7788	0.70	2.0138	0.4966	1.15	3.1582	0.3166
26	1.2969	0.7711	71	2.0340	0.4916	16	3.1899	0.3135
27	1.3100	0.7634	72	2.0544	0.4868	17	3.2220	0.3104
28	1.3231	0.7558	73	2.0751	0.4819	18	3.2544	0.3073
29	1.3364	0.7483	74	2.0959	0.4771	19	3.2871	0.3042
0.30	1.3499	0.7408	0.75	2.1170	0.4724	1.20	3.3201	0.3012
31	1.3634	0.7334	76	1.1383	0.4677	21	3.3535	0.2982
32	1.3771	0.7261	77	2.1598	0.4630	22	3.3872	0.2952
33	1.3910	0.7189	78	2.1815	0.4584	23	3.4212	0.2923
34	1.4049	0.7118	79	2.2034	0.4538	24	3.4556	0.2894
0.35	1.4191	0.7047	0.80	2.2255	0.4493	1.25	3.4903	0.2865
36	1.4333	0.6977	81	2.2479	0.4449	26	3.5254	0.2837
37	1.4477	0.6907	82	2.2705	0.4404	27	3.5609	0.2808
38	1.4623	0.6839	83	2.2933	0.4360	28	3.5966	0.2780
39	1.4770	0.6771	84	2.3164	0.4317	29	3.6328	0.2753
0.40	1.4918	0.6703	0.85	2.3396	0.4274	1.30	3.6693	0.2725
41	1.5068	0.6637	86	2.3632	0.4232	31	3.7062	0.2698
42	1.5220	0.6570	87	2.3869	0.4190	32	3.7434	0.2671
43	1.5373	0.6505	88	2.4109	0.4148	33	3.7810	0.2645
44	1.5527	0.6440	89	2.4351	0.4107	34	3.8190	0.2618

x	e^x	e^{-x}	x	e^x	e^{-x}	x	e^x	e^{-x}
1.35	3.8574	0.2592	82	6.1719	0.1620	29	9.8749	0.1013
36	3.8962	0.2567	83	6.2339	0.1604	2.30	9.9742	0.10026
37	3.9354	0.2541	84	6.2965	0.1588	31	10.074	0.09926
38	3.9749	0.2516	1.85	6.3598	0.1572	32	10.176	0.09827
39	4.0149	0.2491	86	6.4237	0.1557	33	10.278	0.09730
1.40	4.0552	0.2466	87	6.4883	0.1541	34	10.381	0.09633
41	4.0960	0.2441	88	6.5535	0.1526	2.35	10.486	0.09537
42	4.1371	0.2417	89	6.6194	0.1511	36	10.591	0.09442
43	4.1787	0.2393	1.90	6.6859	0.1496	37	10.697	0.09348
44	4.2207	0.2369	91	6.7531	0.1481	38	10.805	0.09255
1.45	4.2631	0.2346	92	6.8210	0.1466	39	10.913	0.09163
46	4.3060	0.2322	93	6.8895	0.1451	2.40	11.023	0.09072
47	4.3492	0.2299	94	6.9588	0.1437	41	11.134	0.08982
48	4.3929	0.2276	1.95	7.0287	0.1423	42	11.246	0.08892
49	4.4371	0.2254	96	7.0993	0.1409	43	11.359	0.08804
1.50	4.4817	0.2231	97	7.1707	0.1395	44	11.473	0.08716
51	4.5267	0.2209	98	7.2427	0.1381	2.45	11.588	0.08629
52	4.5722	0.2187	99	7.3155	0.1367	46	11.705	0.08543
53	4.6182	0.2165	2.00	7.3891	0.1353	47	11.822	0.08458
54	4.6646	0.2144	01	7.4633	0.1340	48	11.941	0.08374
1.55	4.7115	0.2122	02	7.5383	0.1327	49	12.061	0.08291
56	4.7588	0.2101	03	7.6141	0.1313	2.50	12.182	0.08208
57	4.8066	0.2080	04	7.6906	0.1300	51	12.305	0.08127
58	4.8550	0.2060	2.05	7.7679	0.1287	52	12.429	0.08046
59	4.9037	0.2039	06	7.8460	0.1275	53	12.554	0.07966
1.60	4.9530	0.2019	07	7.9248	0.1262	54	12.680	0.07887
61	5.0028	0.1999	08	8.0045	0.1249	2.55	12.807	0.07808
62	5.0531	0.1979	09	8.0849	0.1237	56	12.936	0.07730
63	5.1039	0.1959	2.10	8.1662	0.1225	57	13.066	0.07654
64	5.1552	0.1940	11	8.2482	0.1212	58	13.197	0.07577
1.65	5.2070	0.1920	12	8.3311	0.1200	59	13.330	0.07502
66	5.2593	0.1901	13	8.4149	0.1188	2.60	13.464	0.07427
67	5.3122	0.1882	14	8.4994	0.1177	61	13.599	0.07353
68	5.3656	0.1864	2.15	8.5849	0.1165	62	13.736	0.07280
69	5.4195	0.1845	16	8.6711	0.1153	63	13.874	0.07208
1.70	5.4739	0.1827	17	8.7583	0.1142	64	14.013	0.07136
71	5.5290	0.1809	18	8.8463	0.1130	2.65	14.154	0.07065
72	5.5845	0.1791	19	8.9352	0.1119	66	14.296	0.06995
73	5.6407	0.1773	2.20	9.0250	0.1108	67	14.440	0.06925
74	5.6973	0.1755	21	9.1157	0.1097	68	14.585	0.06856
1.75	5.7546	0.1738	22	9.2073	0.1086	69	14.732	0.06788
76	5.8124	0.1720	23	9.2999	0.1075	2.70	14.880	0.06721
77	5.8709	0.1703	24	9.3933	0.1065	71	15.029	0.06654
78	5.9299	0.1686	2.25	9.4877	0.1054	72	15.180	0.06587
79	5.9895	0.1670	26	9.5831	0.1044	73	15.333	0.06522
1.80	6.0496	0.1653	27	9.6794	0.1033	74	15.487	0.06457
81	6.1104	0.1637	28	9.7767	0.1023			

x	e^x	e^{-x}	x	e^x	e^{-x}	x	e^x	e^{-x}
2.75	15.643	0.06393	22	25.028	0.03996	69	40.045	0.02497
76	15.800	0.06329	23	25.280	0.03956	3.70	40.447	0.02472
77	15.959	0.06266	24	25.534	0.03916	71	40.854	0.02448
78	16.119	0.06204	3.25	25.790	0.03877	72	41.264	0.02423
79	16.281	0.06142	26	26.050	0.03839	73	41.679	0.02339
2.80	16.445	0.06081	27	23.311	0.03801	74	42.098	0.02375
81	16.610	0.06020	28	26.576	0.03763	3.75	42.521	0.02352
82	16.777	0.05961	29	26.843	0.03725	76	42.948	0.02328
83	16.945	0.05901	3.30	27.113	0.03688	77	43.380	0.02305
84	17.116	0.05843	31	27.385	0.03652	78	43.816	0.02282
2.85	17.288	0.05784	32	27.660	0.03615	79	44.256	0.02260
86	17.462	0.05727	33	27.933	0.03579	3.80	44.701	0.02237
87	17.637	0.05670	34	28.219	0.03544	81	45.150	0.02215
88	17.814	0.05613	3.35	28.503	0.03508	82	45.604	0.02193
89	17.993	0.05558	36	28.789	0.03474	83	46.063	0.02171
2.90	18.174	0.05502	37	29.079	0.03439	84	46.525	0.02149
91	18.357	0.05448	38	29.371	0.03405	3.85	46.993	0.02128
92	18.541	0.05393	39	29.666	0.03371	86	47.465	0.02107
93	18.728	0.05340	3.40	29.964	0.03337	87	47.942	0.02086
94	18.916	0.05287	41	30.265	0.03304	88	48.424	0.02065
2.95	19.106	0.05234	42	30.569	0.03271	89	48.911	0.02045
96	19.298	0.05182	43	30.877	0.03239	3.90	49.402	0.02024
97	19.492	0.05130	44	31.187	0.03206	91	49.899	0.02004
98	19.688	0.05079	3.45	31.500	0.03175	92	50.400	0.01984
99	19.886	0.05029	46	31.817	0.03143	93	50.907	0.01964
3.00	20.086	0.04979	47	32.137	0.03112	94	51.419	0.01945
01	20.287	0.04929	48	32.460	0.03081	3.95	51.935	0.01925
02	20.491	0.04880	49	32.786	0.03050	96	52.457	0.01906
03	20.697	0.04832	3.50	33.115	0.03020	97	52.985	0.01887
04	20.905	0.04783	51	33.448	0.02990	98	53.517	0.01869
3.05	21.115	0.04736	52	33.784	0.02960	99	54.055	0.01850
06	21.328	0.04689	53	34.124	0.02930	4.0	54.598	0.01832
07	21.542	0.4642	54	34.467	0.02901	1	60.340	0.01657
08	21.758	0.04596	3.55	34.813	0.02872	2	66.686	0.01500
09	21.977	0.04550	56	35.163	0.02844	3	73.700	0.01357
3.10	22.198	0.04505	57	35.517	0.02816	4	81.451	0.01228
11	22.421	0.04460	58	35.874	0.02788	4.5	90.017	0.01111
12	22.646	0.04416	59	36.234	0.02760	6	99.484	0.01005
13	22.874	0.04372	3.60	36.598	0.02732	7	109.95	0.00910
14	23.104	0.04328	61	36.966	0.02705	8	121.51	0.00823
3.15	23.336	0.04285	62	37.338	0.02678	9	134.29	0.00745
16	23.571	0.04243	63	37.713	0.02652	5.0	148.41	0.00674
17	23.807	0.04200	64	38.092	0.02625	1	164.02	0.00610
18	24.047	0.04158	3.65	38.475	0.02599	2	181.27	0.00552
19	24.288	0.04117	66	38.861	0.02573	3	200.34	0.00499
3.20	24.535	0.04076	67	39.252	0.02548	4	221.41	0.00454
21	24.779	0.04036	68	39.646	0.02522			

x	e^x	e^{-x}	x	e^x	e^{-x}	x	e^x	e^{-x}
5.5	244.69	0.00409	2	1339.4	0.000747	9	7332.0	0.000136
6	270.43	0.00370	3	1480.3	0.000676	9.0	8103.1	0.000123
7	298.87	0.00335	4	1636.0	0.000611	1	8955.3	0.000112
8	330.30	0.00303	7.5	1808.0	0.000553	2	9897.1	0.000101
9	365.04	0.00274	6	1998.2	0.000500	3	10938.0	0.000091
6.0	403.43	0.002479	7	2208.3	0.000453	4	12088.0	0.000083
1	445.86	0.002243	8	2440.6	0.000410	9.5	13360	0.000075
2	492.75	0.002020	9	2697.3	0.000371	6	14765	0.000068
3	544.57	0.001836	8.0	2981.0	0.000335	7	16318	0.000061
4	601.85	0.001662	1	3294.5	0.000304	8	18034	0.000055
6.5	665.14	0.001503	2	3641.0	0.000275	9	19930	0.000050
6	735.10	0.001360	3	4023.9	0.000249	10.0	22026	0.000045
7	812.41	0.001231	4	4447.1	0.000225	20	4.85×10^8	2.1×10^{-9}
8	897.85	0.001114	8.5	4914.8	0.000203	30	1.07×10^{13}	9.3×10^{-14}
9	992.27	0.001008	6	5431.7	0.000184	40	2.35×10^{17}	4.2×10^{-18}
7.0	1096.6	0.000912	7	6002.9	0.000167	50	5.18×10^{21}	1.93×10^{-22}
1	1212.0	0.000825	8	6634.2	0.000151			

14. DECAY AND ACCUMULATION OF RADIOACTIVE ISOTOPE *

$t/T_{1/2}$	$e^{-\lambda t}$	$(1 - e^{-\lambda t})$	$t/T_{1/2}$	$e^{-\lambda t}$	$(1 - e^{-\lambda t})$
0.02	0.985	0.015	0.40	0.758	0.242
0.04	0.972	0.028	0.42	0.748	0.252
0.06	0.959	0.041	0.44	0.737	0.263
0.08	0.946	0.054	0.46	0.727	0.273
0.10	0.933	0.067	0.48	0.717	0.283
0.12	0.920	0.080	0.50	0.707	0.293
0.14	0.907	0.093	0.55	0.683	0.317
0.16	0.894	0.106	0.60	0.659	0.341
0.18	0.882	0.118	0.65	0.637	0.363
0.20	0.870	0.130	0.70	0.615	0.385
0.22	0.858	0.142	0.75	0.594	0.406
0.24	0.846	0.154	0.80	0.574	0.426
0.26	0.835	0.165	0.85	0.555	0.445
0.28	0.823	0.177	0.90	0.536	0.464
0.30	0.812	0.188	0.95	0.518	0.482
0.32	0.801	0.199	1.00	0.500	0.500
0.34	0.790	0.210	1.05	0.483	0.517
0.36	0.779	0.221	1.10	0.467	0.533
0.38	0.769	0.231	1.15	0.451	0.549

$t/T_{1/2}$	$e^{-\lambda t}$	$(1-e^{-\lambda t})$	$t/T_{1/2}$	$e^{-\lambda t}$	$(1-e^{-\lambda t})$
1.20	0.435	0.565	2.60	0.165	0.835
1.25	0.420	0.580	2.70	0.154	0.846
1.30	0.406	0.594	2.80	0.144	0.856
1.35	0.392	0.608	2.90	0.134	0.866
1.40	0.379	0.621	3.00	0.125	0.875
1.45	0.366	0.634	3.20	0.109	0.891
1.50	0.354	0.646	3.40	0.095	0.95
1.60	0.330	0.670	3.60	0.083	0.917
1.70	0.308	0.692	3.80	0.072	0.928
1.80	0.288	0.712	4.00	0.062	0.938
1.90	0.268	0.732	4.20	0.054	0.946
2.00	0.250	0.750	4.40	0.047	0.953
2.10	0.233	0.767	4.60	0.041	0.959
2.20	0.218	0.782	4.80	0.036	0.964
2.30	0.203	0.797	5.00	0.031	0.969
2.40	0.190	0.810			
2.50	0.177	0.823			

* t — time of accumulation for the decay of a radioactive element; $T_{1/2}$ — half-life of the radioactive element; λ — decay constant.

15. MANTISSAS OF COMMON LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	9	13	17	22	26	30	35	39
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	12	16	20	24	28	32	36
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	11	15	18	22	26	29	33
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1699	1729	3	5	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	4	8	11	14	17	20	23	26
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	3	7	10	13	16	19	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3	2	6	9	12	15	18	20	23
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	1	5	8	11	14	16	18	20
19	2788	2810	2832	2856	2878	2900	2923	2945	2967	2989	2	0	4	7	9	11	14	16	18
20	3010	3032	3054	3075	3096						2	0	3	6	8	11	13	15	17

21	3222	3243	3263	3284	3304	3118	3139	3160	3181	3201	2	4	6	8	10	12	14	17	19
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	16	18
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	13	14
29	4623	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	4	5	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	6	7	8	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	7	8	9
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	8	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8	9
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	3	4	5	6	7	8
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	3	4	5	6	7	8
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	3	4	5	6	7	8
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	3	4	5	6	7	8
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	3	4	5	6	7	8
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	3	4	5	6	7	8
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	3	4	5	6	7	8
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	3	4	5	6	7	8
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	3	4	5	6	7	8
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	3	4	5	6	7	8
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	7	8
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	6	7	8
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	6	7	8
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	6	7	8
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	6	7	8
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	6	7	8
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	5	6	7	8
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	3	3	4	4	4	4	4
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	4	4	4
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	4	4	4
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	4	4	4
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	4	4	4
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	4	4	4
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	4	4	4	4	4
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	4	4	4	4	4

77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9166	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9378	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9350	9400	9405	9410	4415	9240	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9953	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4

$$\pi = 3.141\,593\,6+; \quad \log \pi = 0.4971; \quad 1/\pi = 0.318\,309\,8+; \quad \log (1/\pi) = 1.5029.$$

$$\sqrt{2} = 1.414\,213\,5+; \quad \log \sqrt{2} = 0.1505; \quad \sqrt{3} = 1.332\,050\,8+; \quad \log \sqrt{3} = 0.2386.$$

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